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ON BILIRUBIN, THE RED COLORING-MATTER OF THE BILE.

BY W. R. ORNDORFF AND J. E. TEEPLE.

1. Preparation and Analyses of Bilirubin.

All the bilirubin used in this work was obtained from ox-gallstones furnished by Armour & Co., of Chicago. We desire to express our thanks to this firm for their kindness and our appreciation of the interest they have taken in the investigation, during which we have used over a pound of the stones. Nearly all of them were bilirubin calcium stones, very few were composed of calcium carbonate and none were cholesterin stones. After being removed from the gall-bladder, they were drained, dried at 100° and then sent to us. The method of separation of the bilirubin from the gallstones first adopted was to thoroughly dry the stones at 100°, powder and sift through a 30-mesh sieve, extract with ether in a Soxhlet apparatus until exhausted (12–20 hours), dry again and

exhaust with chloroform in the same way (30–40 hours). The material was then dried once more to remove the chloroform, placed in a large evaporating dish and extracted with successive portions of boiling, distilled water until exhausted. This method of procedure removed fat, lecithin, cholesterin, uncombined bilirubin and other bile pigments soluble in ether or chloroform and bile or other substances soluble in water. The material remaining, which had a deep red color, was then digested for several hours with *excess* of very dilute hydrochloric acid, washed by decantation until the filtrate ceased to give any reaction either for calcium or for chlorides; dried thoroughly and extracted in a Soxhlet apparatus, first with ether (2 hours), then with absolute alcohol, until the alcoholic filtrate had only a faint yellow color, (6 hours) and finally with pure chloroform until exhausted (125 hours). Fresh chloroform was used every 8 hours and all extractions and other work with this solvent and bilirubin were done in a photographic dark-room.

The chloroform extracts, containing the bilirubin, were concentrated by distilling off the excess of chloroform on the water-bath, the bilirubin was precipitated by absolute alcohol and the mixture heated on the water-bath until most of the chloroform had been removed. The alcohol was then decanted and the precipitated bilirubin boiled repeatedly with absolute alcohol until exhausted, in order to remove the so-called biliverdin, biliprasin, bilifuscin and any other soluble material.

The product thus obtained was found not to be *completely* soluble in chloroform,[1] though it left no ash when burned and the amount which did not go into solution was very small. It was therefore boiled with large quantities of chloroform, in successive portions, the solution filtered twice, to remove suspended matter, concentrated, precipitated with absolute alcohol,

[1] In nearly all prolonged extractions with the Soxhlet apparatus we found that the extracted material was not entirely soluble in the solvent used. This is probably due to some of the substance being carried over mechanically.

washed with alcohol, filtered, dried and if not completely soluble in chloroform, the process was repeated.

With one lot of gallstones the following results were obtained: 130 grams of the stones, dried at 100°, gave 8 grams of ether extract, 5.2 grams of chloroform extract, 9.5 grams of water extract, 20 grams of hydrochloric acid extract, 1.1 grams of ether extract, 2 grams of alcoholic extract and 22.5 grams of the crude bilirubin. The residue (about 60 grams) consisted of the so-called bilihumin.

Some of the product, completely soluble in chloroform, was then recrystallized twice from dimethylaniline (b. p. 192°.2–192°.8). This specimen crystallized in beautiful reddish-yellow, minute needles and, under the microscope, appeared perfectly homogeneous and free from amorphous matter. A mixture of 2 parts chloroform and 1 part dimethylaniline gave even better crystals (see Fig. III.). Chloroform solution of quinine was also found to dissolve large quantities of the bilirubin, which separated in crystals nearly as good as the preceding ones.

Analyses:

1. Bilirubin crystallized *twice* from dimethylaniline, completely soluble in chloroform and leaving no ash, dried at 120°.

0.269 gram bilirubin gave 17.7 cc. N/10 NH_3 or 0.02485 gram N. Kjeldahl-Gunning method, modified to include nitrogen of nitrates, as adopted by the Association of Official Agricultural Chemists, 1898.[1]

2. Same product and method as No. 1. Digested three-quarters of an hour longer than No. 1.[2]

0.3444 gram bilirubin gave 22.7 cc. N/10 NH_3 or 0.03187 gram N.

3. Product like No. 1, but a different preparation. First reduced the bilirubin with zinc and sulphuric acid and then

[1] Bulletin 46 (revised) U. S. Department of Agriculture, Division of Chemistry, p. 17.

[2] Analyses 1 and 2 were made by Professor G. W. Cavanaugh, Chemist of the Agricultural Experiment Station at Cornell University, to whom we wish to express our thanks.

used the Kjeldahl-Gunning method, adopted also by the Association of Official Agricultural Chemists. Product dried at 125°.

0.2977 gram bilirubin gave 19.07 cc. N/10 NH_3 or 0.02679 gram N.

4. Product like No. 1, but a different preparation. First reduced the bilirubin by the action of P_2I_4 and H_2O (Chenel[1]), then used the Kjeldahl-Gunning method. Product dried at 125°.

0.2158 gram bilirubin gave 14.12 cc. N/10 NH_3 or 0.01982 gram N.

5. Product like the preceding ones but a different preparation (Dumas method). Carbon dioxide generated in a Kipp apparatus from marble that had been thoroughly boiled in water to expel air. Carbon dioxide ran three to four hours to expel all air. Product dried at 130°.

0.2208 gram bilirubin gave 19.2 cc. N, 732 mm. (cor.) and 24°.5.

6. Same product and method as No. 5.

0.1728 gram bilirubin gave 15.25 cc. N, 729.8 mm. (cor.) and 26°.

7. Mixture of what remained of products 3 to 6 (Dumas method). Carbon dioxide generated from boiled, supersaturated sodium bicarbonate solution and boiled, dilute sulphuric acid.

0.1659 gram bilirubin gave 14.2 cc. N, 733.95 mm. (cor.) and 25°.8.

8. Product recrystallized from dimethylaniline, not completely soluble in chloroform but leaving a negligible residue, dried at 130°. Dumas method, using magnesite and heating it in a separate combustion tube, on a short furnace. The copper oxide and the copper spiral were heated for some time in a current of carbon dioxide and allowed to cool in this gas, in order to get rid of occluded air, hydrogen, or carbon monoxide.[2]

[1] Bull. Soc. Chim., 1892, (1), p. 321.

[2] Following a suggestion of Prof. H. N. Morse of the Johns Hopkins University.

0.1659 gram bilirubin gave 14.2 cc. N, 748.8 mm. (cor.) and 27°.[1]

9. Product precipitated from chloroform by alcohol, completely soluble in chloroform, dried at 130°. Same method as No. 8.

0.2084 gram bilirubin gave 17.45 cc. N, 742 mm. (cor.) and 24°.

10. Same product as No. 9, method as given in Gattermann. Employed a copper spiral, which was reduced in methyl alcohol and then heated in a current of carbon dioxide before use, to expel occluded hydrogen or carbon monoxide.

0.2050 gram bilirubin gave 0.5048 gram CO_2 and 0.1133 gram H_2O.

11. Same product as No. 8. Same method as No. 10.

0.2336 gram bilirubin gave 0.5761 gram CO_2 and 0.1248 gram H_2O.

12. Same product as Nos. 9 and 10. Method of Benedict,[2] using a weighed amount of rock candy to furnish the reduced copper. Dried at 140°.

0.2594 gram bilirubin and 0.1270 gram sugar gave 0.8300 gram CO_2 and 0.2078 gram H_2O. CO_2 from the sugar; calculated 0.1960 gram; H_2O from the sugar; calculated 0.07355 gram, leaving 0.6340 gram CO_2 and 0.13425 gram H_2O from the bilirubin.

13. Same product and method as No. 12.

0.3025 gram bilirubin and 0.1348 gram sugar gave 0.9504 gram CO_2 and 0.23995 gram H_2O. CO_2 from the sugar, calculated 0.2080 gram; H_2O from the sugar; calculated 0.07805 gram, leaving 0.7424 gram CO_2 and 0.1619 gram H_2O from the bilirubin.

14. Same product as Nos. 9, 10, 12 and 13. Analysis made by Prof. Benedict, using his own method.

0.1504 gram bilirubin and 0.1126 gram sugar gave 0.5411 gram CO_2 and 0.1543 gram H_2O. CO_2 from the sugar; calculated 0.1737 gram; H_2O from the sugar; calculated 0.0652

[1] Analysis No. 7 was made Feb. 23, 1901; analysis No. 8 April 27, 1901.

[2] THIS JOURNAL, **23**, 343. According to Benedict, the reduced copper spiral, as ordinarily used, might contain enough carbon dioxide or other carbon compound to vitiate the results.

gram, leaving 0.3674 gram CO_2 and 0.0891 gram H_2O from the bilirubin.

15. Same product and method as No. 14. Analysis made by Prof. Benedict.

0.1512 gram bilirubin and 0.1017 gram sugar gave 0.5253 gram CO_2 and 0.1409 gram H_2O; CO_2 from the sugar; calculated 0.1569 gram; H_2O from the sugar; calculated 0.0589 gram, leaving 0.3684 gram CO_2 and 0.0820 gram H_2O from the bilirubin.

16. Same product as No. 14 and 15. Determination made by method used in cases in which the nitrogen is in the unoxidized condition.[1]

0.1245 gram bilirubin gave 0.2990 gram[2] CO_2 and 0.0675 gram H_2O.

The sugar used in experiments 14 and 15 gave the following results:

0.2026 gram gave 0.3123 gram CO_2 and 0.1181 gram H_2O.

	Calculated.	Found.
C	42.07	42.04
H	6.49	6.50

Summary of Results.[3]

No.	Nitrogen.	No.	Carbon.	Hydrogen.
1	9.24	10	67.15	6.18
2	9.25	11	67.25	5.99
3	9.10	12	66.66	5.80
4	9.19	13	66.93	5.99
5	9.36	14	66.62	6.63(?)
6	9.39	15	66.45	6.07
7	9.17	16	65.50(?)	6.07
8	9.31			
9	9.16			

	Nitrogen.	Carbon.	Hydrogen.
Averages[4]	9.24	66.84	6.02
Calculated for $C_{16}H_{18}N_2O_3$	9.81	67.08	6.34
" " $C_{34}H_{36}N_4O_7$	9.17	66.61	5.94

[1] THIS JOURNAL, **23**, 337.

[2] Tube broke before completion of the analysis.

[3] The international atomic weights (O = 16) have been used throughout this paper.

[4] The percentages of carbon in No. 16 and hydrogen in No. 14 are omitted in this average.

The above analyses were made on seven different preparations, by three men, using seven variations of methods for determining the nitrogen and three modifications for the carbon and hydrogen. The more refined and accurate the method of analysis used, the greater seemed to be the divergence from the percentages required for the formula $C_{16}H_{18}N_2O_3$. In the earlier stages of this work we thought that the bilirubin might be impure. To obtain a pure product we therefore used every precaution that had ever been suggested, besides some additional ones. Most of the determinations were made with crystallized products, which appeared perfectly homogeneous when examined under the microscope. No amorphous matter could be detected in the mass of crystals and only one kind of crystals was present. These all had the same extinction angle. The bilirubin, precipitated from chloroform by alcohol, the product which Städeler and Maly analyzed, gave us practically the same results as the crystallized products such as Küster and von Zumbusch analyzed. Analysis No. 1 was made on the first crystals and No. 5 on the last ones from the same dimethylaniline with successive portions of bilirubin dissolved in it. There was, therefore, no evidence of a fractional separation from this solvent. We sometimes noticed when dissolving, in chloroform, a product precipitated from chloroform by alcohol, that one portion of the material seemed to dissolve more readily than another, but we attributed this to differences in the mechanical state of division. So far as we could determine, the finer particles of the bilirubin went into solution in the chloroform first, leaving the coarser material undissolved.

From the descriptions of bilirubin given in the literature, our products compared very favorably, in purity, with the best that any previous investigators had obtained and the analyses certainly indicated this.

Difficulties in analyzing such substances are frequently encountered, for example, von Zumbusch[1] states that he could get no ammonia at all from bilifuscin by any of the Kjeldahl

[1] Z. physiol. Chem., 31, 454.

methods, although the compound gave over 8 per cent of nitrogen by the absolute method. This appears all the more astonishing in view of the fact that he found he could determine the amount of nitrogen in bilirubin by the Kjeldahl method. Nencki and Zaleski[1] found that haemin and haematoporphyrin require heating for hours at a white heat to give off all the nitrogen and, when analyzed by the Kjeldahl method, the digestion must be continued for some hours after the fluid is decolorized. We expected to find such difficulties here and after the first two analyses, by the Kjeldahl method, had failed to give the amount of nitrogen required by the formula $C_{16}H_{18}N_2O_3$, we tried all the methods mentioned above. Bilirubin is very resistant to the usual analytical treatment. Prolonged heating at a high temperature, using a Jena glass combustion tube, is essential to obtain all the nitrogen by the Dumas method and vigorous reduction and lengthy digestion with sulphuric acid and potassium sulphate, after the fluid has been decolorized, are necessary in determining the nitrogen by the Kjeldahl method. Notwithstanding all these precautions, however, none of the determinations had given as much as 9.4 per cent of nitrogen (while the theory demanded 9.81 per cent) and we were satisfied that there was no more than this in the substance. Likewise, in the carbon and hydrogen determinations, we regarded those made by Benedict's method as most accurate because there were fewer sources of error. The average of these results, including those made by Professor Benedict and our own, was C 66.66 and H 5.98 per cent; the theory for $C_{16}H_{18}N_2O_3$ required 67.08 and 6.34 per cent, respectively.

As, therefore, we had no reason to suspect the analytical results and as our product seemed homogeneous and as pure as those of previous investigators, we examined all the analyses of bilirubin which had been published and upon which was based the commonly accepted formula, $C_{16}H_{18}N_2O_3$, first ascribed to it by Städeler, in 1864. The following are the results of all the analyses published between that time and 1902:

[1] Z. physiol. Chem., **30**, 387.

Investigator.		C.	H.	N.	Remarks.
Städeler (1864)		67.15	6.27	9.59	N. by the soda-lime method.
		67.11	6.12		Bilirubin precipitated from chloroform by alcohol.
Thudichum (1868)		66.02	5.97	9.05	N. by the absolute method.
		66.41	6.13	9.49	N. by the soda-lime method.
		65.61	5.95	8.82	
					Bilirubin precipitated from chloroform by alcohol.
Maly (1868)		67.16	6.18		Bilirubin precipitated from chloroform by alcohol.
			6.22		
" (1874)		67.52	6.29		
		66.95	6.29		
Küster (1898)	I.	66.94	7.03	11.48	N. by the absolute method.
		66.99	6.88	11.35	Bilirubin crystallized from dimethylaniline.
	II.	67.45	6.77	10.21	Only the last of the three products was both free from ash and completely soluble in chloroform.
	III.	67.19	6.46	10.12	
Von Zumbusch (1900)				9.30	Bilirubin crystallized from dimethylaniline. N. by the Kjeldahl method.
Average of all analyses on products soluble in chloroform and free from ash		66.79	6.19	9.39	
Average found by us		66.84	6.02	9.24	
Theory for $C_{16}H_{18}N_2O_3$		67.08	6.34	9.81	
Theory for $C_{24}H_{28}N_4O_7$		66.61	5.94	9.17	

In Hoppe-Seyler's "Handbuch der physiol. und pathol. chemischen Analyse," H. Thierfelder, seventh edition, p. 287, the following statement occurs: "Die Zusammensetzung und die Eigenschaften des Bilirubins sind von Städeler festgestellt worden. Maly hat diese Angaben bestätigt und die Analysen von Hoppe-Seyler lassen gleichfalls keinen Zweifel an der Richtigkeit der Städelerschen Formel." We have been unable to find any record of these analyses of Hoppe-Seyler.

The greatest difference between our results and the theoretical values for the formula $C_{16}H_{18}N_2O_3$, occurs in the nitrogen, where it amounts to 6 per cent of the total. Examining the previous nitrogen determinations, we find that Städeler based his formula on but one and that by the, now obsolete, "soda-lime" method. Thudichum's results vary too widely to carry much weight and only one of his nitrogen determinations was made by the absolute method, their average, however, is still lower than ours. Maly did not determine the nitrogen in the bilirubin he analyzed. Küster's four values for nitrogen are all much higher than the theory requires (from 3 to 17 per cent of the total) and only the last of his three products was *both* completely soluble in chloroform and free from ash. Von Zumbusch's analysis, by the Kjeldahl method, agrees with ours. A comparison of the averages of all analyses, on products completely soluble in chloroform and free from ash, with the averages found by us, shows them to be practically identical.

We were, therefore, convinced that bilirubin, the pigment occurring in ox-gallstones, soluble in chloroform, alkalies and dimethylaniline, practically insoluble in alcohol, ether and petroleum ether, prepared by any of the methods heretofore used, did not have the composition represented by the formula $C_{16}H_{18}N_2O_3$. These results were published in July, 1901, in a preliminary paper,[1] with the provisional statement that they agreed better with the formula $C_{34}H_{36}N_4O_7$ than with any other.

In consequence of the publication of our work Küster[2] was led to re-examine the pigment (April, 1902). Working with

[1] THIS JOURNAL, **26**, 86.

[2] Ber. d. chem. Ges., **35**, 1268.

a large quantity of material, 1000 grams of the dried ox-gallstones and 200 grams of biliary concrement obtained from a horse, he was able to demonstrate that what has, hitherto, been called bilirubin is a mixture of *at least two* substances, differing only in their degree of solubility in chloroform and in their percentage composition. He also states in a foot-note, "Die Resultate von Orndorff und Teeple (Amer. Chem. Jour., **26**, 87) erklären sich vielleicht durch einen Gehalt ihres Bilirubins an leichter löslichen Farbstoff."

For the product least soluble in chloroform he retains the name bilirubin and his analyses of this compound, recrystallized from dimethylaniline, give results which now agree remarkably well with those demanded by the formula $C_{16}H_{18}N_2O_3$, though he unfortunately omits all analytical data. The more soluble compound he was not able to obtain pure, but he found, in a general way, from the products which he analyzed, that it contained less nitrogen and usually less carbon, than the substance for which he retains the name bilirubin.

As stated above, we had repeatedly observed these differences in the solubility of the various products in chloroform, but had attributed them to differences in the mechanical state of division of the products, supposing that the finer material dissolved and left the coarser. We now repeated the work and were able to confirm Küster's statement regarding the presence of two substances in the chloroform extract which differed only in the degree of their solubility in this solvent. Our method of obtaining the bilirubin from the gallstones was the same as Küster's, except that we subjected the material to an exhaustive extraction with alcohol before treatment with chloroform and that we did not deem it wise, in extracting, to use such small amounts of chloroform that the bilirubin separated in crusts, nor did it seem best to crystallize the material from a solvent with a boiling-point so high as that of dimethylaniline. We therefore exhausted the material with large amounts of chloroform, filtered, distilled off a part of the solvent on the water-bath and allowed the liquid to cool slowly. The crystalline product, which separates after standing for a day or two, was filtered, boiled with alcohol and re-

peatedly recrystallized, in the same manner, from large amounts of chloroform. This method gives a perfectly pure crystalline product, entirely free from the material more soluble in chloroform. It has, of course, the disadvantage that large quantities of chloroform are required. The product, however, is much superior to that obtained in any other way. The analyses were made with bilirubin obtained in this way and dried to constant weight at 123°:

1. 0.1438 gram substance gave 12.5 cc. N at 20°.5 and 753.8 mm. (cor.) Absolute method. Carbon dioxide from magnesite.

2. 0.1557 gram substance gave 13.3 cc. N at 19°.8 and 749.5 mm. (cor.) Absolute method. Carbon dioxide from magnesite.

3. 0.1592 gram substance gave 10.9 cc. of N/10 ammonia. Kjeldahl-Gunning method after first reducing with zinc dust and sulphuric acid.[1]

4. 0.1607 gram substance gave 11.18 cc. of N/10 ammonia. Kjeldahl-Gunning method after first reducing with P_2I_4 and water.

Summary.

No.	Nitrogen.
1	9.83
2	9.65
3	9.60
4	9.77
Calculated for $C_{16}H_{18}N_2O_3$	9.81

These results, together with those recently published by Küster, show, beyond all doubt, that the formula of the compound less soluble in chloroform is $C_{16}H_{18}N_2O_3$ and that all analyses recorded up to 1902 were made on a mixture of this less soluble bilirubin, with a small amount of another substance closely resembling it in all respects, except that it contained a lower percentage of nitrogen and was more soluble in chloroform.

Whether the pure bilirubin thus isolated occurs in fresh bile is unknown.[2]

[1] This analysis was made for us by Professor G. W. Cavanaugh of the Agricultural Experiment Station at Cornell University.

[2] *Vide* Thudichum: Virchow's Arch., **156**, 384 (1900).

2. *Properties of Bilirubin.*

a. Crystallization and Crystal Form.—Amorphous bilirubin, precipitated from chloroform by alcohol, is red, when crystallized from dimethylaniline or chloroform the color is deep-red; the thinner crystals, observed under the microscope, are yellowish-red by transmitted light.

Bilirubin has weak acidic properties, somewhat like those of the phenols; it dissolves readily in dilute solutions of the alkalies and alkaline carbonates, more slowly in concentrated solutions, particularly of the alkaline carbonates. Carbon dioxide precipitates it, almost completely, in the amorphous form, from solution in dilute alkalies. The chloroform solution of the pigment is completely decolorized by shaking with dilute alkali solution. Solution of bilirubin in ammonia does not reduce ammoniacal silver nitrate even when boiled, indicating that the substance does not contain an aldehyde group.

Bilirubin may be crystallized from dimethylaniline, from a mixture of dimethylaniline and chloroform, or, best, from chloroform alone. The crystals from dimethylaniline are usually cigar shaped[1] and incompletely formed, those from a mixture of dimethylaniline and chloroform are more perfect (see Fig. III.). If the bilirubin has been carefully purified from the more soluble product, the best crystals may be obtained from chloroform (see Figs. I., II. and IV.).[2] The older statement that bilirubin crystallizes best from impure solutions is certainly wrong. When perfectly pure, a drop of a chloroform solution of bilirubin, allowed to evaporate spontaneously, deposits nothing but crystallized material. Two specimens, crystallized from chloroform, were submitted to Prof. A. C. Gill, of the Mineralogical Department of Cornell University, who reports as follows: "The crystals are columnar in shape, with the end faces almost at right angles to the direction of elongation. They are monoclinic or triclinic, probably the former, as judged from the very indefinite optical figure in converged polarized light. They have an extinction

[1] *Vide* Küster: Z. physiol. Chem., **26**, 325 for an illustration of these crystals.

[2] We desire to express our thanks to Prof. S. H. Gage, of Cornell University, for these four photographs.

angle of 9°–10°, show high double refraction and slight pleochroism. The color of the thinnest crystals is orange-yellow, that of the thickest brick-red. The material seemed to be entirely crystalline, as no amorphous matter was observed. All the crystals have the same extinction angle, which also indicates that they are probably monoclinic, the columnar shape being due to the development of the prism." When a drop of a saturated solution of *pure* bilirubin, in chloroform, is allowed to evaporate on a microscope slide, part of the crystals formed are rectangular tablets, like those described above, the remainder consists of long elliptical needles, the whole field (plates and needles), however, has the same extinction angle.

With regard to the crystals from a mixture of dimethylaniline and chloroform, Dr. Gill reports as follows: "The crystals form stout needles or elongated columns, having an orange-yellow color and showing a distinct, but not strong, pleochroism. The ends are, in some cases, sharply terminated by faces, inclined about 60° to the direction of elongation. Most of these crystals do not extinguish between crossed Nicols, thus indicating a strong dispersion or, more likely, a twin structure, which is not apparent from their external form. Some of those with broken ends show strong double refraction and sharp extinction, at an angle varying from 2°.5 to 12°. The crystals are either monoclinic or triclinic, as shown by this extinction angle."

b. Solubility.—Thudichum gives the solubility of bilirubin as 1 in 586 parts of chloroform, while Küster found it to be 1 : 567. Neither investigator describes his method of determining the solubility or, indeed, gives any details. Pure, crystallized bilirubin dissolves very slowly in chloroform, even when boiled for some time. In order to prepare a saturated solution we found it was best to boil the bilirubin with chloroform (using an upright condenser) for 8–12 hours, filter, distil off a portion of the solvent on the water-bath and let the liquid stand till next day. Crystals of bilirubin slowly separate and rise to the surface. If the amount of bili-

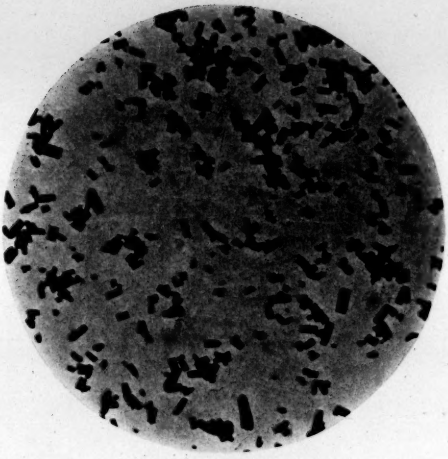


Fig. I.—Bilirubin crystallized from chloroform. Magnified 390 times.

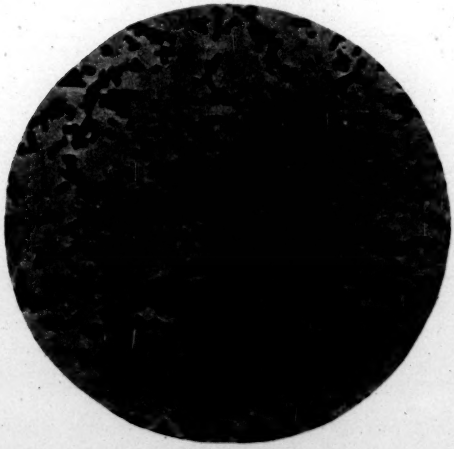


Fig. II.—Bilirubin crystallized from chloroform. Magnified 390 times.

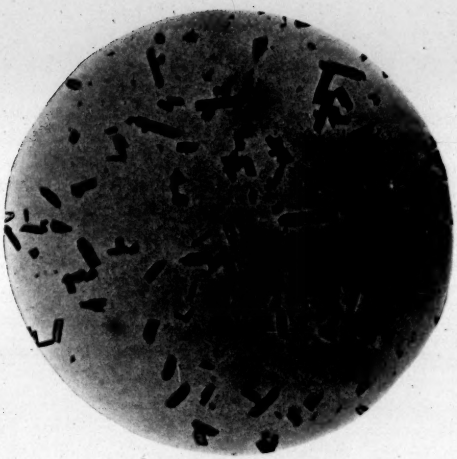


Fig. III —Bilirubin crystallized from a mixture of dimethylaniline and chloroform. Magnified 330 times.

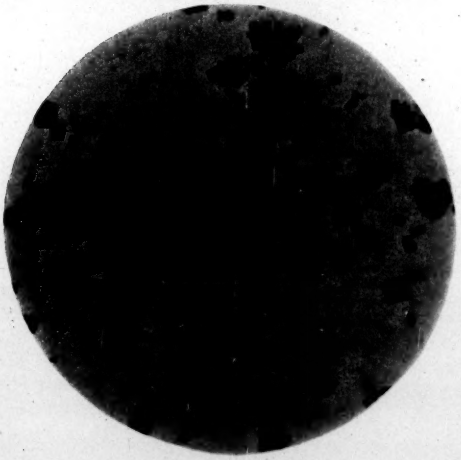


Fig. IV.—Bilirubin crystallized from chloroform by cooling very slowly. Magnified 330 times.

rubin present in this solution be determined by removing the crystals and evaporating a weighed quantity of the filtrate to dryness on the water-bath, the solubility will be found to be very nearly the same as given by Thudichum and Küster, provided the solution has only stood in contact with the crystals a few hours. This does not, however, represent the true solubility of bilirubin in chloroform, for, when the liquid is allowed to stand longer in contact with the crystals, more are deposited, showing that the solution is still supersaturated. The condition of equilibrium is not reached for several days at least. The following results were obtained by the method described above. After the mixture had stood the required length of time, a small portion of the solution was filtered from the crystals, weighed, evaporated to dryness on the water-bath and the residual bilirubin also weighed. The remainder of the solution was allowed to stand in contact with the crystals for several days longer, when another portion was treated in the same manner. The solubility was determined at 23° :

Experiment.	Time the solution stood with crystals. Days.	Weight of the solution in grams.	Weight of bilirubin in grams.	Solubility, 1 part in
1	1	32.42	0.0479	676
	6	23.259	0.0263	884
2	5	26.83	0.0303	884
	12	20.902	0.0208	1004
3	10	39.886	0.0409	974

We attempted to get a saturated solution of bilirubin in chloroform by boiling 0.3 gram of pure, crystallized material, for 4 hours, with 45 grams of chloroform, in a reflux apparatus. After filtering the cold solution we found that 29.534 grams of it gave 0.0296 gram bilirubin, corresponding to 1 part in 997 parts of chloroform.

In order to avoid the formation of supersaturated solutions we endeavored to determine the solubility of the bilirubin in chloroform by shaking the two in sealed tubes. The following results were obtained by Mr. F. C. Robinson, to whom we wish to express our thanks :

Time of contact.	Weight of solution in grams.	Weight of bilirubin in grams.	Solubility, 1 part in
10 days shaking and 3 days standing	11.12	0.00286	3887
10 days shaking and 34 days standing	2.97	0.00115	2582

Temperature, 20°.1.

From these results it will be seen that the tendency of bilirubin to form supersaturated solutions, in chloroform, is very great and that the determination of its solubility in this medium is a matter of considerable difficulty.

Chloroform solution of anhydrous quinine dissolves much larger quantities of bilirubin than chloroform alone, and when the solution evaporates spontaneously, fairly good crystals are deposited, some being well formed, others imperfect, like those from dimethylaniline. The bilirubin may also be precipitated from the chloroform-quinine solution by absolute alcohol.

We endeavored to determine the molecular weight of pure bilirubin in the chloroform-quinine solution by the ebullioscopic method, but without success, as the addition of bilirubin caused no perceptible rise in the boiling-point of the solution, probably because the bilirubin combined with the quinine and so did not increase the number of molecules present.

When bilirubin is fused with potassium hydroxide it gradually dissolves, forming, finally, a colorless liquid and evolving small amounts of ammonia and of a pyrrol derivative, as was shown by the fact that the vapors slowly turned red litmus paper blue and reddened a pine splinter, which had been moistened with hydrochloric acid.

3. *Attempts to Determine the Presence of Alkyloxy and Alkylimide Groups in Bilirubin.*

Bilirubin does not contain an alkyloxy group, as was shown by the fact that, when treated with *pure* hydriodic acid, according to the Zeisel method[1] for determining alkyloxy groups, the amount of silver iodide formed was practically unweighable.

[1] Monats. Chem., 6, 989.

Attempts to determine whether it contains an alkylimide group, by Herzig and Meyer's[1] method, by heating with hydriodic acid and ammonium iodide, did not result so decisively. The sources of error in the method itself are so considerable that the authors acknowledge it to be unreliable where the molecular weight of the substance, in which the alkylimide group is to be determined, is larger than 600. We show, later, that the molecular weight of bilirubin is 572. The following are the results which we obtained :

No.	Weight of bilirubin.	Weight silver iodide.	Per cent CH_3.	Theory for one CH_3 group in $C_{33}H_{36}N_4O_6$.
1	0.3125	0.1200	2.46	2.62
2	0.2845	0.1018	2.29	
3	0.2912	0.0966	2.12	
4	0.2338	0.0515	1.41	
5	0.1921	0.0267	0.89	

Products 1 and 2 were crystallized from dimethylaniline ; they were prepared in the same way as products 1, 2 and 3, the results of the analysis of which are given on p. 217. Apparently they are not entirely free from the substance more soluble than bilirubin, containing a smaller amount of nitrogen; they may have contained a little dimethylaniline, though they were dried at 120° before being analyzed. Product No. 3 was precipitated from chloroform solution by alcohol and was the same as products 9 and 10, the results of the analysis of which are given on p. 219. It was dried at 130° before analysis. Products 4 and 5 were pure bilirubin, carefully crystallized from chloroform and dried at 123° ; they were the same products as those, 1, 2, 3 and 4, analyses of which are given on p. 219. The *purest* products give the *smallest* percentages for the methyl group and all the results are below the value required for one methyl group to the molecule $C_{33}H_{36}N_4O_6$. It is highly probable, therefore, that *pure* bilirubin does not contain a methylimide group, though the method seems hardly accurate enough to decide this point absolutely, in the case of a compound with such a large molecular weight.

[1] Monats. Chem., **15**, 613.

4. Reduction of Bilirubin.

a. With Zinc Dust.—Bilirubin (1.2 grams) was thoroughly mixed with zinc dust (25 grams), by grinding in a mortar and the mixture carefully heated in a current of hydrogen, in a hard-glass combustion tube, to which was attached a Peligot tube surrounded by ice-water. Greenish-yellow vapors were evolved, which partially condensed to a yellow liquid in the Peligot tube. They had an alkaline reaction and reddened a pine splinter moistened with hydrochloric acid.

When passed through solution of mercuric chloride they gave a precipitate which had all the characteristics of haemopyrrol-mercuric chloride; it dissolved completely in alcohol containing hydrochloric acid and this solution rapidly became colored and showed the urobilin spectrum.

Part of the yellow liquid dissolved in water and gave a white precipitate with Nessler's reagent. On standing, this yellow liquid changed to a dark-brown resinous mass and the Peligot tube acquired a very marked odor of an old pipe. All these properties indicate that the yellow liquid contained haemopyrrol, which was also obtained, later, by the reduction of bilirubin with nascent hydriodic acid.

b. With Sodium Amalgam.—Considerable quantities of bilirubin (over 4 grams) and various bilirubin residues were repeatedly reduced with sodium amalgam, according to Städeler and Maly's[1] directions. The product resulting agreed, generally, in properties with Maly's so-called hydrobilirubin; it gave the same absorption band, the characteristic reaction with zinc chloride and the specific reaction with iodic acid described by Capranica.[2] It did not seem to us, however, to be a uniform substance and exhibited somewhat different properties when slight changes were made in the method of preparation. We found it impossible to purify the material by recrystallization from any solvent and consequently no further work was done with it. Incidentally, it was noticed that the addition of bromine water to an aqueous alcoholic solution of the "hydro-

[1] Ann. Chem. (Liebig), 161, 368; 163, 77.
[2] Jahres. Thierchemie, 12, 302.

bilirubin" decolorized the solution and gave a very voluminous yellow precipitate.

c. With Nascent Hydriodic Acid.—Nencki and Zaleski[1] obtained haemopyrrol, $C_8H_{13}N$, by reducing acethaemin, and Nencki and Marchlewski[2] made the same product from phyllocyanin, a derivative of chlorophyll, thus establishing a very close relationship between the blood and plant coloring-matters. Later, Küster[3] found that Mörner's β-haeminal so gave haemopyrrol, when reduced by Nencki's method. In all these cases the substances were reduced by heating, in glacial acetic acid solution, with hydriodic acid (sp. gr. 1.96) and phosphonium iodide.

As bilirubin is, in all probability, derived from the haemoglobin of the blood, we naturally expected to obtain haemopyrrol from it by reduction. Our experiments on the reduction of bilirubin with zinc dust had shown, indeed, that haemopyrrol could also be obtained from bilirubin, but this method only gave a small yield and the product was hardly pure enough for analysis.

In determining the nitrogen in bilirubin, by the Kjeldahl-Gunning method, we found that a previous reduction with phosphorus tetraiodide and water (the Chenel method) was essential in order, subsequently, to obtain complete oxidation by the sulphuric acid, within any reasonable length of time. Supposing that the bilirubin was here, also, reduced to haemopyrrol, we made a number of experiments with acethaemin to perfect the method and compare the results with Nencki's.

The best procedure was the following: Phosphorus (2 grams) was dissolved in carbon disulphide (about 20 cc.) in a long-necked Kjeldahl flask[4] and iodine (16 grams) was added slowly, in small portions, shaking thoroughly after each addition until solution is complete. When all the iodine has

[1] Ber. d. chem. Ges., **34**, 1003.

[2] *Ibid.*, **34**, 1689.

[3] *Ibid.*, **35**, 2953.

[4] Chenel recommends the use of the phosphorus and iodine in the ratio of 1:6, but we obtained better results when we used 1:8, nearly those theoretically required for the compound P_2I_4. If Chenel's directions are followed, a separation of amorphous phosphorus often occurs when the compound is decomposed with water.

been added and is combined with the phosphorus, the carbon disulphide is distilled at as low a temperature as possible and the last traces of it removed from the crystals of phosphorus tetraiodide by a current of *dry* air. Add the acethaemin (0.2–0.5 gram) and mix thoroughly by shaking with the phosphorus tetraiodide which is then decomposed by hot water (8–10 cc.). The flask is heated on the water-bath for 2–3 minutes, thoroughly shaken, and the liquid prevented from foaming over, by cooling, if necessary. Hydriodic acid and phosphonium iodide are formed and rapidly reduce the substance, which goes completely into solution, yielding, finally, a light yellow liquid. After cooling, the solution is diluted with a little water, partly neutralized with sodium carbonate and enough sodium acetate solution added to combine with the remaining acids, leaving only a small amount of acetic acid free. The mixture is then distilled in a current of carbon dioxide, the distillate being collected in solution of mercuric chloride. The precipitate of mercury haemopyrrol mercuric chloride, $(C_8H_{12}N)_2Hg.(HgCl_2)_4$, is filtered, washed with water, dried over sulphuric acid and weighed.

Analysis by Nencki and Zaleski's[1] method:

0.2742 gram mercury compound gave 0.2089 gram HgS.

Percentage of mercury found	65.66
Computed for $(C_8H_{12}N)_2Hg.(HgCl_2)_4$	65.45

This indicates that the product formed by this method of reduction, is identical with the haemopyrrol obtained by Nencki and his co-workers from acethaemin and phyllocyanin and by Küster from β-haemin. This was also indicated by the fact that solutions of the compound turn red on standing and then show the very distinct and characteristic absorption band, the "urobilin" spectrum, exactly as solutions of haemopyrrol do.

If we assume, with Küster,[2] that the molecule of haematin consists of two parts, as shown in the scheme

R—R'—Fe—R'—R

[1] Ber. d. chem. Ges., **34**, 1003.

[2] Ann. Chem. (Liebig), **315**, 184 (1900).

and that only the radicals R are converted into haemopyrrol by reduction, or into the haematinic acids by oxidation, as haemopyrrol and the haematinic acids come from the same part of the molecule,[1] then 1 molecule of acethaemin should yield, on reduction, 2 molecules of haemopyrrol, or 1 molecule of the mercuric chloride double salt, $(C_8H_{13}N)_2Hg.(HgCl_2)_4$, that is, 1 gram of acethaemin should yield 2.345 grams of the mercuric derivative, or 0.3773 gram of haemopyrrol. The best yield we obtained was as follows: 0.54 gram acethaemin gave 0.53 gram of the mercuric chloride double salt, which is equivalent to 42 per cent of the theoretical amount.

Küster[2] states that he obtained 2 grams of the mercury compound from 5 grams of the β-haemin, equivalent to 0.7 gram of haemopyrrol. One of these figures is evidently a misprint, for the 2 grams of mercury compound correspond to 17.45 per cent of the amount required by theory, while the 0.7 gram of haemopyrrol is equivalent to 37.9 per cent of the theoretical. Nencki and Zaleski[3] once obtained 32 per cent of the calculated amount, on the assumption that each molecule of acethaemin yields 4 molecules of haemopyrrol. They do not give the weight of the mercury compound obtained, however and so it is impossible to recalculate their results.

The reason why a larger yield of haemopyrrol is not obtained, is undoubtedly due to the fact that it polymerizes or oxidizes so readily. If we attempt to distil the haemopyrrol with steam, instead of using carbon dioxide, the liquid rapidly darkens, a resinous mass precipitates, and the yield is much diminished. The liquid from which the haemopyrrol has been distilled then shows a very pronounced "urobilin" absorption band. This same change takes place very rapidly when the haemopyrrol solution is allowed to stand, so that it is advisable to distil off the haemopyrrol as soon as the reduction of the acethaemin is completed. This polymerization or resinifying of the haemopyrrol takes place, to some extent, whatever precautions are taken to prevent it, as the liquid left in the distillation-flask always shows the

[1] Ber. d. chem. Ges., **35**, 2953 (1902).
[2] *Ibid.*, **35**, 2953 (1902).
[3] *Ibid.*, **34**, 1006.

"urobilin" absorption band. Various unsuccessful attempts were made to precipitate the haemopyrrol mercury compound directly from the filtered solution, without distilling.

The filtrate from the mercury derivative gradually turns red on standing and the liquid then shows the "urobilin" absorption band. It is evident, therefore, that the haemopyrrol is not completely precipitated from solution by the mercuric chloride. This would also diminish the yield of haemopyrrol.

Some residues from the precipitation of bilirubin from chloroform by alcohol, which had a marked red color, though they may have contained some biliverdin and some of the compound more soluble in chloroform, were reduced according to the method described above. To 0.34 gram of the residue we used 3.4 grams of phosphorus and 27.2 grams of iodine and obtained a very light yellow solution. When this was partly neutralized with sodium carbonate, sodium acetate added and distilled in a current of carbon dioxide, the distillate gave a precipitate with mercuric chloride exactly like that resulting from the acethaemin. The liquid remaining in the flask also became dark colored—almost black—on standing and showed the "urobilin" spectrum. When the precipitate with the mercuric chloride solution was examined, it was found to be different from the haemopyrrol-mercuric chloride precipitate obtained from the acethaemin. Only a small part of it was soluble in alcoholic hydrochloric acid, whereas the haemopyrrol-mercuric chloride precipitate completely dissolves. The solution of the mercuric chloride compound in the alcoholic hydrochloric acid behaved exactly like that of the haemopyrrol-mercuric chloride compound, however, rapidly becoming colored and showing the "urobilin" spectrum. The amount of the precipitate was small and the greater part was evidently not the haemopyrrol-mercuric chloride derivative. Similar precipitates were obtained from pure bilirubin, from the compound more soluble in chloroform, from the green "biliverdin" and also from the "bilihumin," the residues in the Soxhlet thimble after extraction with chloroform. All these substances seem to yield small quantities of haemopyrrol on reduction. Bilirubin is much more resistant to the action of reducing agents than acethaemin.

5. Azo Compounds of Bilirubin.

Ehrlich[1] found, in 1883, that benzenediazonium sulphonate reacts very readily with bilirubin, the product being red in neutral, weakly alkaline, or faintly acid solutions. With strong hydrochloric acid it is beautifully blue and in strong alkalies greenish-blue. None of the other pigments found in the bile gave this reaction. In 1900 Pröscher[2] combined bilirubin with acetophenonediazonium chloride and isolated the product, which he named acetophenoneazobilirubin.

As it was highly probable, from our work on the reduction of bilirubin, that it was a derivative of pyrrol, we expected to get here two compounds, a monazo and a disazo derivative, as O. Fischer and Hepp[3] had found to be the case with pyrrol and its homologues. Investigation soon showed that this supposition was correct. By means of these compounds we hoped to be able to determine the molecular weight and formula of bilirubin.

Tribromaniline was the base selected from which to make the diazonium compound, as the amount of bromine which it contains is so large that it is very easy, by simply making a bromine determination, to distinguish between the monazo and the disazo derivatives. If the formula of bilirubin is $C_{16}H_{18}N_2O_3$, we should expect the tribromdiazonium salt to combine with it in accordance with the following equations:

(1) $C_6H_2Br_3N_2HSO_4 + C_{16}H_{18}N_2O_3 = C_6H_2Br_3N_2C_{16}H_{17}N_2O_3 + H_2SO_4$

(2) $2C_6H_2Br_3N_2HSO_4 + C_{16}H_{18}N_2O_3 = (C_6H_2Br_3N_2)_2C_{16}H_{16}N_2O_3 + 2H_2SO_4$,

while, if the molecule of bilirubin is represented by the formula $C_{32}H_{36}N_4O_6$, the equations would be:

(3) $C_6H_2Br_3N_2HSO_4 + C_{32}H_{36}N_4O_6 = C_6H_2Br_3N_2C_{32}H_{35}N_4O_6 + H_2SO_4$

(4) $2C_6H_2Br_3N_2HSO_4 + C_{32}H_{36}N_4O_6 = (C_6H_2Br_3N_2)_2C_{32}H_{34}N_4O_6 + 2H_2SO_4$.

[1] Z. anal. Chem., **23**, 275 (1883).
[2] Z. physiol. Chem., **29**, 411.
[3] Ber. d. chem. Ges., **19**, 2251.

The formulas of the resulting compounds, their molecular weights and the percentages of bromine they contain are shown below:

	Formula.	Molecular weight.	Percentage of bromine.
1	$C_{22}H_{19}N_4O_3Br_3$	627.23	38.244
2	$C_{33}H_{30}N_6O_3Br_6$	968.16	49.55
3	$C_{35}H_{27}N_6O_6Br_3$	913.49	26.26
4	$C_{44}H_{38}N_8O_6Br_6$	1254.46	38.244

If the two azo compounds can be shown to contain 26.26 and 38.24 per cent of bromine respectively, then the formula of bilirubin must be $C_{33}H_{36}N_4O_6$. Compounds 1 and 4 contain the same amount of bromine and it is impossible to distinguish between them by analysis. The molecular weight of 4, however, is double that of 1.

The tribromaniline was made according to the method of Fritzsche, as given by Silberstein[1] and also by the one recommended by Jackson and Bancroft.[2] Both gave a product, which, when purified, melted at 119° and was free from other bromine derivatives of aniline as shown by analyses:

I. 0.3051 gram tribromaniline gave 0.5225 gram AgBr.
II. 0.1999 gram tribromaniline gave 0.3410 gram AgBr.

	Calculated for $C_6H_2Br_3NH_2$.	Found. I.	Found. II.
Br	72.70	72.89	72.60

Analysis I. was made by the Carius method; II. by heating with lime.

In the earlier experiments the tribromaniline was diazotized by means of nitrogen trioxide, according to Silberstein's directions, but after the publication of Hantzsch and Jochem's[3] article, their much superior method was alone used. The tribrombenzenediazonium acid sulphate was beautifully crystallized and pure white. It was dried over sulphuric acid before use. After many trials, we found the following to be the best method of preparation of the azo compounds: dissolve about 2 grams of pure bilirubin, by heating with 800–900 cc. of chloro-

[1] J. prakt. Chem., [2], **27**, 100 (1883).
[2] THIS JOURNAL, **12**, 290 (1890).
[3] Ber. d. chem. Ges., **34**, 3337 (1901).

form in a flask connected with a reflux condenser, cool the solution to 8° and add 250 cc. of absolute alcohol. Then dissolve about 3.5 grams of the *freshly* prepared tribrombenzenediazonium acid sulphate in 10–15 cc. of cold distilled water and add this solution to the first one, shake thoroughly, add more alcohol, if necessary, to make a homogeneous solution and allow to stand until the liquid has assumed the room temperature. The addition of the diazonium salt causes a marked change in color, the liquid finally becoming deep-red. Now add a large excess of distilled water; the chloroform separates, carrying with it the azo compounds, while the alcohol and the excess of the diazonium salt dissolve in the water; the latter is siphoned off and the chloroform washed repeatedly with large amounts of water in order to remove the alcohol. During this washing a precipitate gradually forms, consisting chiefly of the monazo product which was held in solution by the alcohol. The chloroform, after separation from the water, is filtered and shaken with about 500 cc. of 2 per cent potassium hydroxide solution to remove the azo compounds. A small amount of tribrombenzene, formed by the interaction of some of the tribrombenzene diazonium acid sulphate with the alcohol, remains in the chloroform. The potassium hydroxide solution of the azo compounds is separated from the chloroform and washed with some fresh chloroform to remove all the tribrombenzene; the azo compounds are then completely precipitated by adding slight excess of dilute sulphuric acid, washed with water by decantation, until the wash water is free from sulphates, filtered and dried. During the washing the wash waters remain nearly colorless until the sulphates are almost entirely removed, then a little of the azo compound seems to go into solution.

The large excess of diazonium salt used was for the purpose of combining with *all* the bilirubin and also because some of it is decomposed by the alcohol. It was hoped that, by the use of a large excess of diazonium salt, it would be possible to convert the bilirubin entirely into the disazo product. Some monazo compound was always formed, however, no matter how the conditions were varied. 1.1 grams of bilirubin gave 1.8 grams of the azo derivatives, consisting chiefly of the disazo product.

The separation of the two azo compounds is long and tedious. Ethyl acetate gave the best results. After several trials we adopted the following method: The powdered mixture of the azo compounds is placed in a paper thimble, in the Soxhlet apparatus and extracted with ethyl acetate (free from acetic acid) until soluble red compounds are removed. Most of the monazo compound remains and the greater part of the disazo compound dissolves. The extract is filtered, concentrated, and, on standing, some material separates which consists chiefly of the monazo compound; it is filtered and the evaporation continued, removing the monazo compound each time as it precipitates, until, finally, the material which separates consists chiefly of the disazo compound. It is easy to distinguish the monazo and disazo compounds, the former gives a red and the latter a beautiful purple color with potassium hydroxide.

The solution remaining is evaporated to dryness on the water-bath, the residue powdered and redissolved in as small an amount of ethyl acetate as possible, filtered, concentrated (the monazo product being removed as it separates) and finally evaporated to dryness. The whole process is then repeated until the residue dissolves *completely* in ethyl acetate. The product may then be recrystallized from ethyl acetate or precipitated from this solution by means of petroleum ether. In some cases we evaporated the ethyl acetate solution to dryness, dissolved the residue in 2 per cent potassium hydroxide, precipitated with dilute sulphuric acid, washed free from sulphates, filtered and dried.

The pure monazo compound is nearly insoluble in ethyl acetate, but in the presence of the disazo product a part of it always goes into solution. A fairly good separation can be effected by using chloroform, but as the monazo compound is more soluble in this than in the ethyl acetate, the separation is much slower and not so complete. The two azo compounds may also be separated by dissolving them in 2–3 per cent potassium hydroxide solution and passing excess of carbon dioxide. The disazo compound precipitates first leaving most

of the monazo compound in solution. Here again, however, the separation is not complete unless the process is repeated four or five times, as some of the disazo compound remains in the carbonate solution and some of the monazo product precipitates. Of the specimens finally obtained for analysis, No. 1 was purified by the ethyl acetate method, No. 2 by dissolving in 2 per cent potassium hydroxide and precipitating with carbon dioxide, repeating the process four times and using large volumes of alkali. The products were dried at 100°.

Analytical results:

I. 0.1348 gram substance gave 0.1202 gram AgBr (Carius).

II. 0.1070 gram substance gave 0.0954 gram AgBr, heating with lime.

0.1640 gram substance gave 10.31 cc. N/10 NH_3. Material first reduced by the Chenel method, then oxidized by the Kjeldahl-Gunning method.

	Calculated for $C_{28}H_{34}N_4O_6(C_6H_3Br_2N_2)_2$.	Found. I.	II.
Br	38.24	37.95	37.94
N	8.95	. .	8.83

An attempt was made to obtain measurable crystals of the disazo compound from glacial acetic acid, in which it is very soluble and from which it crystallizes beautifully, in large, well-formed rosettes, easily visible to the naked eye. The crystals were very dark, almost black, with a peculiar bronze luster. When dried, however, they lost weight steadily for a long time, even in the water-oven and the bromine determinations invariably came a little low. Whether this was due to the presence of acetic acid of crystallization, to the formation of acetyl compounds, or to loss of bromine we were unable to determine. From the slowness with which the compound lost weight we were inclined to regard it as an acetyl derivative of the disazo product. One specimen, dried to constancy at 112°, steadily decreased in weight during 50 hours and had then lost approximately the equivalent of 4 molecules of acetic acid to 1 of the disazo compound. This substance was analyzed.

I. 0.1228 gram substance gave 0.1048 gram AgBr. Percentage of bromine 36.31.

II. 0.1016 gram substance gave 0.0866 gram AgBr. Percentage of bromine 36.27.

These values show that the compound had lost bromine as well as acetic acid, or that all the acetic acid had not been removed. At higher temperatures the loss was greater and the dried product was changed in character, so that the work with it was discontinued. Even in the case of the *purest* products obtained from ethyl acetate there seemed to be a steady loss of bromine if the substance was heated for any length of time above 100°.

The other azo derivative, which we have called the monazo compound, was obtained by collecting the material precipitating out of the chloroform solutions of the mixed azo products, when these were washed with water, and also the substance deposited from the ethyl acetate solutions of the azo compounds during concentration. The mixture was powdered, placed in the paper thimble containing the azo product insoluble in ethyl acetate and the whole re-extracted with ethyl acetate. The extract was concentrated and any monazo compound which separated was collected and again extracted. This process was continued until a product was obtained almost insoluble in chloroform or ethyl acetate, more soluble in alcohol and soluble in dilute alkalies with a *red* color. When a specimen dissolved in alkalies with a pure red color, the solution giving no absorption band,[1] it was assumed to be pure and free from the disazo derivative, as we found it impossible to crystallize it from any solvent. Some of the preparations seemed to be contaminated with a product containing a smaller amount of bromine, possibly a decomposition-product of the monazo compound itself; this could be partially removed by extracting the substance with alcohol, but, if the extraction were continued too long, the monazo compound was dissolved

[1] As will be shown later, the *disazo* compound gives a very marked and characteristic absorption band in acid or alkaline solution, while the monazo product gives none.

and, in any case, there was considerable loss of the latter by this method of purification. The total amount of monazo product which we obtained was small and we were therefore not able to purify it perfectly. Analyses of specimens dried at 105° :

I. 0.0950 gram substance gave 0.0567 gram AgBr. Heating with lime.

II. 0.0814 gram substance gave 0.0486 gram AgBr (Carius).

	Calculated for $C_{33}H_{36}N_4O_6(N_2C_6H_2Br_3)$.	Found. I.	II.
Br	26.26	25.40	25.41

These results show that the compound must be a monazo derivative, having the formula $C_{33}H_{35}N_4O_6(N_2C_6H_2Br_3)$ and hence that the formula of bilirubin itself must be $C_{33}H_{36}N_4O_6$.

Some products were obtained which gave a higher percentage of bromine, but an examination of their alkaline solutions showed the absorption band so characteristic of the disazo product, hence these analyses were discarded.

Several attempts were made to prepare the monazo compound by mixing bilirubin with the calculated amount of tribrombenzenediazonium salt, but without success, as a mixture of the two azo derivatives was always formed. Even when we mixed 10 cc. of concentrated hydrochloric acid with the chloroform-alcohol solution of 2 grams of bilirubin, before the solution of the diazonium salt was added, the result was the same. We also endeavored to make the disazo compound exclusively, by allowing the diazonium salt to remain in contact with the bilirubin solution over night, but here again a mixture of the two azo compounds was always obtained.

The results from the analyses of the disazo product agree just as well with the formula for the monazo derivative,

$$C_6H_2Br_3N_2C_{16}H_{17}N_2O_3,$$

(see p. 238) as they do for that of the disazo compound,

$$(C_6H_2Br_3N_2)_2C_{32}H_{34}N_4O_4.$$

That this product is a disazo compound, however, seems to be proved from the following considerations :

1. It gives a fine blue color with concentrated hydrochloric or sulphuric acid, the monazo compound gives a red color with these reagents. This is in accord with the statements made by O. Fischer and E. Hepp regarding the conduct of disazo and monazo compounds of pyrrol and its homologues towards strong acids.

2. The fact that this product is formed in largest quantity when an *excess* of the diazonium salt is present, is also an indication that it is a disazo and not a monazo compound.

3. We made many unsuccessful attempts to isolate a product from the mixture of the azo compounds containing more bromine than this one.

As will be seen from the table on p. 238, if the disazo compound has the formula $(C_6H_2Br_3N_2)_2C_{16}H_{16}N_2O_3$, the percentage of bromine would be 49.55, whereas the highest percentage we found in any azo compound was only 37.95. Moreover, as shown above, by the action of tribrombenzenediazonium acid sulphate on bilirubin we obtained an azo compound which contains 25.4 per cent of bromine, dissolves in concentrated hydrochloric or sulphuric acid with a red color and which must, therefore, be the monazo compound,

$$C_6H_2Br_3N_2C_{32}H_{35}N_4O_6.$$

As the disazo compound is fairly soluble in chloroform and in ethyl acetate, we endeavored to confirm, by molecular weight determinations, the view of its composition given above, using the Landsberger-McCoy apparatus:

Solvent, Chloroform.

Disazo product. Grams.	Solution. cc.	Rise in boiling-point.	Molecular weight found.	Molecular weight calculated for $C_{22}H_{24}N_4O_3(C_6H_2Br_3N_2)_2$.
1.15 (742–741.2 mm.)	11.2	0°.207	1289	1254.46
	13.9	0°.147	1463	
	17.8	0°.130	1292	
	19.3	0°.135	1148	
0.9763 (746 mm.)	8.6	0°.207	1426	For $C_{18}H_{17}N_3O_3(C_6H_2Br_3N_2)$. 627.23
	12.1	0°.153	1371	
	16.3	0°.122	1276	
	23.8	0°.086	1240	
0.526 (747–746.9 mm.)	11.8	0°.079	1467	

Solvent Ethyl Acetate.

Disazo product. Grams.	Solution. cc.	Rise in boiling-point.	Molecular weight found.
0.2675	8.4	0.096	1042

(Bar. 742 mm.)

These values indicate that the disazo compound has a molecular weight of 1254.46, which corresponds to the formula $C_{32}H_{34}N_4O_6(C_6H_2Br_3N_2)_2$. Bilirubin itself must, then, have the formula $C_{32}H_{36}N_4O_6$.

Owing to the very high molecular weight of the disazo compound and the great difficulty of dissolving it, as well as its slight solubility in the solvents used, we do not lay too much stress on these molecular weight determinations; they are recorded, however, just as they were made and the results agree with those obtained from the analyses of the azo compounds. Attention should, perhaps, be called to the fact that these conclusions are in accord with Maly's on tribrombilirubin,[1] hydrobilirubin and on the oxidation of bilirubin to biliverdin and also with Abel's determinations of the molecular weight of hydrobilirubin[2] by the cryoscopic method.

According to measurements made for us by Mr. L. F. Hawley, the disazo compound, in alcoholic potassium hydroxide solution, gave a well-defined absorption band between $\lambda = 606$ and $\lambda = 536$. In alcoholic hydrochloric acid the band was between $\lambda = 573.5$ and $\lambda = 495.5$. The latter is weaker and not so well defined as the former.

The following table shows the differences observed between the two azo compounds:

	Disazo compound, $C_{32}H_{34}N_4O_6(C_6H_2Br_3N_2)_2$.	Monazo compound, $C_{32}H_{35}N_4O_6(C_6H_2Br_3N_2)$.
Potassium hydroxide (2 per cent)	Bluish purple	Red
Concentrated hydrochloric acid	" "	Purplish-red
Acids or alkalies	Absorption band	No absorption band
Chloroform	Very soluble	Slightly soluble
Ethyl acetate	Soluble	Insoluble
Carbon disulphide	"	"
KOH solution + CO_2	Precipitates	Remains in solution

[1] Jahresber. u. die Fortsch. der Thierchemie, **5**, 193.
[2] Monats. Chem., **11**, 61 (1890).

In neutral or ammoniacal solution the disazo compound is red and these solutions show no absorption band.

Azo Compounds Formed from Bilirubin with Diazonium Acetophenone Salts.

As has already been stated, Pröscher combined bilirubin with acetophenone diazonium chloride and obtained a compound, crystallizing from chloroform, to which he assigned the formula $C_{34}H_{38}N_4O_4$.

After we discovered that tribrombenzenediazonium acid sulphate combines with bilirubin to form a monazo and a disazo derivative, we decided to repeat Pröscher's work. The method used in making the azo compounds was the same as that employed in making the tribrommonazo and disazo products given above, differing from Pröscher's only in that the acetophenone diazonium acid sulphate was made by Hantzsch and Jochem's method and that it was isolated and purified before use. We found that two azo compounds are also formed here, one, the monazo, not very soluble in chloroform and practically insoluble in carbon disulphide, the other, the disazo derivative, analyzed by Pröscher, quite soluble in these media. Some of the data given by Pröscher differ slightly from ours.

Carbon disulphide is the best solvent for the separation of the two azo compounds. The mixture was extracted in a Soxhlet apparatus with carbon disulphide until the solvent runs off practically colorless. Part of it was then distilled ; on cooling, crystals of the disazo compound separated. More crystals were obtained by further evaporation. These were collected and re-extracted with carbon disulphide. Two or three extractions and crystallizations are sufficient to obtain a pure product. After recrystallizing from carbon disulphide three times, thin, shining crystals, 1–2 mm. in length, were obtained. These were described by Professor A. C. Gill, of the Mineralogical Department of Cornell University, as follows: "The substance crystallizes in elongated, wedge-shaped plates, which are frequently aggregated into rosette-like forms, red by transmitted light, somewhat pleochroic, with purplish and yellowish tinges to the red ; oblique

extinction showing that they are either monoclinic or triclinic. In converged polarized light they show that the tabular faces are not at right angles to any axis of elasticity, hence the crystals are probably triclinic." Another portion, obtained in a similar manner, was described by Dr. Gill as follows: "The groups of yellowish-red to brownish-red, thin, tabular crystals are doubtless triclinic and show pleochroism. An optical axis seems to emerge at a small angle with the normal to the flat face."

Analyses of the product, recrystallized three times from carbon disulphide and dried to constant weight in a water-oven:

I. 0.1599 gram substance gave 19 cc. N at 19° and 739.6 mm. (cor.)

II. 0.0919 gram substance gave 8.49 cc. N/10 NH_3.

	Calculated for $C_{32}H_{34}N_4O_6(C_8H_7N_2O)_2$.	Found. I.	II.
N	12.99	13.29	12.97

Analysis I. was made by the Dumas method; II. by first reducing the compound with phosphorus and iodine (Chenel) and then oxidizing with sulphuric acid and potassium sulphate (Kjeldahl-Gunning method).

The results show that the compound is identical with Pröscher's product.

The monazo compound, insoluble in carbon disulphide and only slightly soluble in chloroform, was exhaustively extracted with these solvents until it was free from the disazo product. This point was quite readily determined by dissolving the monazo compound in alcohol, adding some potassium hydroxide and examing the solution with the spectroscope. The slightest trace of the disazo compound may be detected by the very marked absorption band. When the monazo compound was freed from the disazo product it was dissolved in alcohol, filtered and evaporated to dryness on the water-bath. Only a small quantity of the pure monazo compound was obtained. Its alcoholic solution is red and turns bluish-green on the addition of alkalies; in strong hydrochloric acid the color is deep purple. Analysis of this product, dried to constant weight at 100° (Chenel-Kjeldahl method):

0.0535 gram substance gave 4.56 cc. N/10 NH_3.

	Calculated for $C_{28}H_{26}N_4O_2(C_6H_7N_2O)$.	Found.
N	11.72	11.96

This result shows that the compound is a monazo derivative and that the one analyzed by Pröscher must, therefore, be the disazo compound; he gives it the formula $C_{34}H_{28}N_4O_4$, but this is certainly wrong. Even if we assume the formula, $C_{16}H_{18}N_2O_3$, for bilirubin, the product resulting from the action of the acetophenone diazonium acid sulphate would have the formula $C_{34}H_{34}N_4O_4$, as shown in the following equation:

$$C_{16}H_{18}N_2O_3 + C_6H_7N_2OHSO_4 = C_{16}H_{17}N_2O_3(C_6H_7N_2O) + H_2SO_4.$$

As the formula for bilirubin is undoubtedly $C_{33}H_{36}N_4O_6$, the derivative is certainly a disazo compound and the equation representing the reaction is as follows:

$$C_{33}H_{36}N_4O_6 + 2C_6H_7N_2OHSO_4 = C_{33}H_{34}N_4O_6(C_6H_7N_2O)_2 + 2H_2SO_4.$$

We give below the results obtained by Pröscher and those required by our formula. We have recalculated Pröscher's values (O = 16).

	Calculated for $C_{28}H_{34}N_4O_4(C_6H_7N_2O)_2$.	Proscher's results.
C	66.61	66.17
H	5.60	6.04
N	12.99	12.97

The disazo compound dissolves in alkali, forming a clear blue solution, which gradually changes to green, then to yellow and finally becomes nearly colorless. Pröscher states that his substance dissolved in alkalies with a green color. Neutral and acetic acid solutions of the disazo product are red, those in concentrated hydrochloric or sulphuric acid are purple or blue, depending on the amount of acid and pigment present.

We obtained almost exactly the same absorption bands as those recorded by Formanek,[1] though we could not pretend to read the maximum points as sharply as he does. We used a

[1] Z. physiol. Chem., 29, 414 (1900).

grating and zirconia light. In alcohol we observed one band with maximum darkness at about $\lambda = 522$; Formanek gives $\lambda = 524.9$. Addition of concentrated hydrochloric acid to the alcoholic solution gives two bands, with a lighter space between, at about $\lambda = 539$; Formanek gives $\lambda = 561.4$ and $\lambda = 525.8$. In alcoholic potassium hydroxide, according to a determination made for us by Dr. Benton Dales, a very marked band is shown with a maximum darkness at $\lambda = 639$; Formanek gives $\lambda = 643.1$.

Substances more Soluble in Chloroform.

Küster has reserved the investigation of the substances in ox-gallstones, which resemble bilirubin very closely, but are more soluble in chloroform and contain less nitrogen, consequently no attempt at a careful study of them was made. In crystallizing crude bilirubin from chloroform, the more soluble products, accumulated in the mother-liquors, may be obtained by evaporation or by precipitation with petroleum ether. Carbon disulphide, methyl alcohol, ethyl alcohol, ethyl acetate, acetone, benzene, toluene and ether all dissolve some of the material and, on concentration, it separates in imperfect microcrystalline masses. Chloroform is the best solvent.

About 1.5 grams of the material were dissolved in a mixture of chloroform and benzene and the solvent gradually evaporated. At a concentration of about 200 cc., when most of the chloroform had volatilized, a considerable amount of red micro-crystalline substance separated. This was removed ; further concentration of the mother-liquor gave a similar precipitate, very much darker in color. Analyses (Chenel-Kjeldahl):

I. 0.1406 gram of the red product gave 9.39 cc. N/10 NH_3.
II. 0.1940 gram of the dark product gave 10.31 cc. N/10 NH_3.

	I.	II.
N	9.38	7.46

Summary.

1. Analyses of the *pure crystallized* bilirubin show that its

composition is correctly represented by the formula $(C_{16}H_{18}N_2O_3)_x$.

2. Bilirubin unites with diazonium compounds, in acid or neutral solutions, forming monazo and disazo derivatives.

3. The monazo compounds have the formula $C_{32}H_{36}N_4O_6(N_2R)$. They are formed in much smaller quantity than the disazo products, are more readily soluble in alkalies and are not precipitated by carbon dioxide. Their solutions show no absorption bands. In most neutral solvents, like carbon disulphide, chloroform and ethyl acetate, they are less soluble than the disazo products.

4. The disazo compounds have the formula $C_{32}H_{34}N_4O_6(N_2R)_2$. They are soluble in alkalies and are precipitated by carbon dioxide. Their solutions show characteristic absorption bands.

5. The existence of these two series of azo derivatives shows that the molecular formula for bilirubin must be $C_{32}H_{36}N_4O_6$.

6. Molecular weight determinations of the tribrombenzene-disazobilirubin are in accord with the results of the analyses of the azo compounds and show that this substance has the formula $C_{32}H_{34}N_4O_6(N_2C_6H_2Br_3)_2$, hence, that the formula of bilirubin is $C_{32}H_{36}N_4O_6$.

7. Bilirubin has acid properties similar to those of the phenols. It is precipitated from alkaline solution by carbon dioxide. It contains no alkyloxy group and probably no alkylimide group. It does not reduce ammoniacal silver nitrate solution, even on boiling, so probably does not contain an aldehyde group. It resembles resorcinol very closely in the manner in which it forms monazo and disazo derivatives.

8. When reduced by zinc dust or nascent hydriodic acid, bilirubin gives haemopyrrol, showing that it is a derivative of pyrrol. The ease with which it forms monazo and disazo compounds, even in the presence of strong acids, points to the same conclusion.

CORNELL UNIVERSITY,
ITHACA, N. Y.,
May, 1904.

Contributions from the Chemical Laboratory of the Case School of Applied Science.

XLV.—ON THE COMPOSITION OF PETROLEUM.[1]

By Charles F. Mabery.

I. THE HYDROCARBONS IN OHIO TRENTON LIMESTONE PETROLEUM.

By Charles F. Mabery and O. H. Palm.

II. THE HYDROCARBONS IN CANADIAN PETROLEUM WITH HIGH BOILING-POINTS.

III. HYDROCARBONS IN SANTA BARBARA CRUDE OIL.

IV. SEPARATION OF SOLID PARAFFIN HYDROCARBONS FROM PETROLEUM WITHOUT DISTILLATION.

By Charles F. Mabery and Otto J. Sieplein.

V. THE SOLID PARAFFIN HYDROCARBONS THAT COLLECT IN OIL WELLS IN PENNSYLVANIA.

VI. COMPOSITION OF COMMERCIAL PARAFFIN.

VII. COMPOSITION OF COMMERCIAL VASELINE, COSMOLINE, AND SIMILAR PRODUCTS.

I. THE HYDROCARBONS IN OHIO TRENTON LIMESTONE PETROLEUM WITH BOILING-POINTS ABOVE 213°.

With O. H. Palm.

In a paper on the constituents of Pennsylvania, Ohio and Canadian petroleum with boiling-points between 150° and 220°,[2] it was shown, as a result of combustion, molecular weight determinations and composition of its chlorine derivatives, that the distillate boiling at 212°–214° from Ohio Trenton limestone petroleum consisted of hendecane, $C_{11}H_{24}$. Study of the portions with higher boiling-points has since been continued for the purpose of ascertaining where the series C_nH_{2n+2} terminates and the series poorer in hydrogen appears.

The higher specific gravity of Trenton limestone petroleum and of the products prepared from it is well known, but the

[1] Aid in this work was given by the American Academy of Arts and Sciences from the C. M. Warren Fund for Chemical Research.

[2] This Journal, 19, 419 (1897).

cause has not yet been explained. Since the series C_nH_{2n+2} has been found to continue, in Pennsylvania petroleum, in the solid forms as high as their molecular weights can be determined and to be associated with series poorer in hydrogen above 260° (50 mm.), it was evidently interesting to ascertain the composition of the higher hydrocarbons in Ohio oil.

Results which will appear later show that the series poorer in hydrogen form the chief portion of Canadiam petroleum; and since the Trenton limestone oil, in its physical properties and in the properties of its distillates, stands in an intermediary position between Pennsylvania and Canadian crude oils, the series of hydrocarbons in Ohio oil should explain the difference in properties of the commercial products obtained from it.

In resuming the study of Ohio Trenton limestone oil in 1901, a barrel of the crude oil was obtained at Welker, Ohio, of sp. gr. 0.8367 at 20°. Analysis gave: C 85.46; H 13.91; S 0.48 per cent.

This crude oil is not so heavy as some specimens from Lima and Indiana and the percentage of sulphur is lower than that of specimens from some other fields, but it was believed to represent an average composition of Trenton limestone oil with reference to the principal series of hydrocarbons.

From 8 liters of the crude oil 1.8 liters were removed, below 200°, under atmospheric pressure; the residue was distilled under 30 mm., at first within limits of 10°, which left a residue, above 280°, of 2,000 grams. Subsequent distillation, under the same pressure, brought the distillates together in larger quantities, within certain well-defined limits of temperature, indicating a greater proportion of individual hydrocarbons. After ten distillations, greater amounts collected within the following limits, and were found to represent definite compounds: 111°–113°; 129°–130°; 138°–140°; 152°–154°; 164°–168°; 177°–179°; 187°–190°; 198°–202°; 213°–216°; 224°–227°; 237°–240°; 253°–255°; 263°–265°; 275°–278°. Although it cannot be assumed that, in a limited number of distillations, the individual hydrocarbons can be separated completely, analysis and molecular weight determinations indicate that the separation is suffi-

cient to admit of identification, not only of members of the same series but of rather sudden changes from one series to the next poorer in hydrogen.

None of the fractions showed evidence of decomposition. The lower fractions were liquid, but the distillate 213°–217° was nearly solid at ordinary temperatures. The higher distillates were completely solid with paraffin, which formed a large part of these fractions. Since the solid hydrocarbons in Pennsylvania petroleum were identified as members of the series C_nH_{2n+2}, and the solid hydrocarbons in Ohio petroleum are, without doubt, composed of the same bodies, it was considered unnecessary to examine these solids from Ohio oil. To remove them the oil was cooled to 0°, filtered, then cooled to —10° and again filtered, under pressure, at the same temperature. In the higher distillates the solid hydrocarbons formed one-third or one-half of each distillate. The oils filtered from these fractions were very thick and viscous; the specific gravity of the unpurified fractions, at 20°, were found to be essentially higher than the corresponding fractions from Pennsylvania oil:

129°-130°.	138°-140°.	152°-154°.	177°-179°.	187°-190°.	198°-202°.
0.7998	0.8065	0.8187	0.8262	0.8351	0.8373
	224°-227°.	237°-240°.		253°-255°.	275°-278°.
(At 50°)	0.8586	0.8622		0.8849	0.8941

After removal of the solid hydrocarbon each fraction was thoroughly purified by agitating, first with common concentrated and then with fuming sulphuric acid until the latter was nearly colorless. The heavier distillates were dissolved, before treatment, in light gasoline; otherwise they formed an emulsion with acid from which the oil did not readily separate. To completely remove the acid the oil was finally washed with sodium hydroxide, then dried over calcium chloride and finally over sodium. If the oil remains unchanged after standing some time over sodium it is very well purified.

In the present state of our knowledge concerning the series of hydrocarbons poorer in hydrogen than the series C_nH_{2n+2}, definite names cannot be assigned to the members of these series. It is probable that the series C_nH_{2n} is composed of the

methylene hydrocarbons, perhaps with complex side chains. The series still poorer in hydrogen may contain two or more methylene rings, but as yet there is no evidence as to the structure of these hydrocarbons.

Hydrocarbon $C_{12}H_{24}$, B. P. 211°–213°.—In a former paper[1] the fraction 212°–214°, under atmospheric pressure, was shown by analysis and further identification to be dodecane $C_{12}H_{26}$, and its sp. gr. was found to be 0.7727 at 20°. This hydrocarbon was separated, with others, from a specimen of crude oil obtained from a well at Findlay, Ohio. Its sp. gr. and composition corresponded to that of dodecane, which was obtained from Pennsylvania petroleum.

The fraction 211°–213°, now under examination, after thorough purification with sulphuric acid, as described above, gave sp. gr. 0.7970.

I. 0.1462 gram oil gave 0.4590 gram CO_2 and 0.1860 gram H_2O.

II. 0.1281 gram oil gave 0.4020 gram CO_2 and 0.1635 gram H_2O.

III. 0.1563 gram oil gave 0.4906 gram CO_2 and 0.2000 gram H_2O.

	Calculated for $C_{12}H_{24}$.	Found. I.	II.	III.
C	85.70	85.62	85.53	85.61
H	14.30	14.25	14.27	14.31

The molecular weight, determined by Beckmann's freezing-point method, in benzene, agreed with that of the formula $C_{12}H_{24}$.

1.1097 grams oil and 29.394 grams benzene gave a depression of 1°.067.

Calculated for $C_{12}H_{24}$.	Found.
168	173

The same formula was verified by the index of refraction, 1.4350, from which the molecular refraction was calculated.

Calculated for $C_{12}H_{24}$.	Found.
54.24	55.00

[1] *Loc. cit.*

It is, therefore, evident that this hydrocarbon has the composition of the series C_nH_{2n}. The only explanation that can be offered as to the difference between it and the product with the same boiling-point separated before, is that the different specimens of oils, coming from different sources, must have differed with respect to this hydrocarbon.

Hydrocarbon $C_{13}H_{26}$, B. P. 123°–125° (30 mm.).—After ten distillations under 30 mm., 27 grams collected at 129°–130°, that distilled, under atmospheric pressure, at 223°–225°. After careful purification the sp. gr. of this distillate was found to be 0.8055 at 20°. It was shown to belong to the series C_nH_{2n}.

I. 0.1536 gram oil gave 0.4824 gram CO_2 and 0.1902 gram H_2O.

II. 0.1336 gram oil gave 0.4195 gram CO_2 and 0.1710 gram H_2O.

	Calculated for $C_{13}H_{26}$.	Found. I.	Found. II.
C	85.70	85.65	85.63
H	14.30	13.85	14.32

The molecular weight, determined at the freezing-point of benzene, corresponded to the formula $C_{13}H_{26}$.

0.9896 gram oil and 25.6727 grams benzene gave a depression of 1°.040.

Calculated for $C_{13}H_{26}$.	Found.
182.0	181.6

A determination of the index of refraction gave 1.4400, which corresponded to the molecular refraction:

Calculated for $C_{13}H_{26}$.	Found.
59.84	59.55

Hydrocarbon $C_{14}H_{28}$, B. P. 138°–140° (30 mm.).—After the tenth distillation 45 grams, collected at 138°–140°, gave sp. gr. 0.8129, at 20°, after thorough purification with acid.

0.1407 gram oil gave 0.4435 gram CO_2 and 0.1787 gram H_2O.

	Calculated for $C_{14}H_{28}$.	Found.
C	85.70	85.96
H	14.30	14.18

The formula was verified by the molecular weight, at the freezing-point of benzene.

0.9552 gram oil and 24.5822 grams benzene gave a depression of 0°.975.

Calculated for $C_{14}H_{28}$.	Found.
196	195.2

The index of refraction was found to be 1.4437 and the molecular refraction agreed with the same formula:

Calculated for $C_{14}H_{28}$.	Found.
64.44	64.10

Hydrocarbon $C_{15}H_{30}$, B. P. 152°–154° (30 mm.).—A fraction of 75 grams, collected at first within these limits, gradually diminished to 20 grams after the tenth distillation. After purification with acid it gave sp. gr. 0.8204 at 20°. Analysis gave values required for the series C_nH_{2n}:

0.1511 gram oil gave 0.4750 gram CO_2 and 0.1920 gram H_2O.

	Calculated for $C_{15}H_{30}$.	Found.
C	85.70	85.74
H	14.30	14.21

The molecular weight, determined at the freezing-point of benzene, corresponded to the formula $C_{15}H_{30}$.

0.9370 gram oil and 24.2115 grams benzene gave a depression of 0°.910.

Calculated for $C_{15}H_{30}$.	Found.
210	208.3

This formula was further confirmed by the index of refraction, 1.4480, which gave the following molecular refraction:

Calculated for $C_{15}H_{30}$.	Found.
69.05	68.50

Hydrocarbon $C_{16}H_{32}$, B. P. 164°–168° (30 mm.).—Eighteen grams of the oil collected within these limits after the tenth distillation that gave sp. gr. 0.8249 at 20°. After filtration at —10°, and purification with acid, the sp. gr. was found to be 0.8254. The proportions of carbon and hydrogen indicated the series C_nH_{2n}.

0.1536 gram oil gave 0.4848 gram CO_2 and 0.1945 gram H_2O.

	Calculated for $C_{16}H_{32}$.	Found.
C	85.70	86.08
H	14.30	14.16

The molecular weight, at the freezing-point of benzene, corresponded to the formula $C_{16}H_{32}$.

1.1300 grams oil and 20.3767 grams benzene gave a depression of 1°.202.

Calculated for $C_{16}H_{32}$.	Found.
224	226

The index found, 1.4510, confirmed the same formula:

Calculated for $C_{16}H_{32}$.	Found.
73.65	73.08

Hydrocarbon $C_{17}H_{34}$, B. P. 177°–179° (30 mm.).—After the tenth distillation 35 grams collected within these limits with sp. gr. 0.8251 at 20°. After filtration at —10° and treatment with acid the sp. gr. was 0.8335. The percentages of carbon and hydrogen indicated the series C_nH_{2n}.

0.1501 gram oil gave 0.4720 gram CO_2 and 0.1881 gram H_2O.

	Calculated for $C_{17}H_{34}$.	Found.
C	85.70	85.76
H	14.30	14.02

The molecular weight, at the freezing-point of benzene, agreed with the formula $C_{17}H_{34}$.

1.0880 grams oil and 24.9900 grams benzene gave a depression of 0°.896.

Calculated for $C_{17}H_{34}$.	Found.
238	238

The index of refraction, 1.4545, supported the same formula:

Calculated for $C_{17}H_{34}$.	Found.
78.25	77.50

A fraction collected at 188°–190° which should contain the next homologous hydrocarbon $C_{18}H_{36}$; the oil was unfortunately lost by an accident during filtration from the solid.

Hydrocarbon $C_{19}H_{38}$, *B. P. 198°–202°* (*30 mm.*).—Thirty grams of this fraction were collected after the tenth distillation, which gave sp. gr. 0.8364 at 20°. On cooling to —10° and filtration, 16 grams of the filtered oil were obtained with sp. gr. 0.8471 at 20°. Determinations of carbon and hydrogen indicated a change from the series C_nH_{2n} to the series C_nH_{2n-2}.

0.1528 gram oil gave 0.4830 gram CO_2 and 0.1845 gram H_2O.

	Calculated for $C_{19}H_{38}$.	Found.
C	86.36	86.24
H	13.64	13.52

A determination of the molecular weight, at the freezing-point of benzene, gave the formula $C_{19}H_{38}$.

0.9063 gram oil and 24.1120 grams benzene gave a depression of 0°.700.

Calculated for $C_{19}H_{38}$.	Found.
264	263

This formula was further verified by its index of refraction, which was found to be 1.4614, corresponding to the molecular refraction:

Calculated for $C_{19}H_{38}$.	Found.
85.35	85.57

Hydrocarbon $C_{21}H_{40}$, *B. P. 213°–217°* (*30 mm.*).—The hy-

drocarbon $C_{20}H_{38}$ was apparently absent, as the distillates were small and did not accumulate below 213°, at which point a larger amount was collected that proved to be the hydrocarbon $C_{21}H_{40}$. After the tenth distillation 25 grams gave sp. gr. 0.8417 at 20°. After filtration at —10° the sp. gr. was 0.8546 at 20°. The carbon and hydrogen corresponded to the series C_nH_{2n-2}.

0.1362 gram oil gave 0.4330 gram CO_2 and 0.1675 gram H_2O.

	Calculated for $C_{21}H_{40}$.	Found.
C	86.30	86.70
H	13.70	13.66

A determination of the molecular weight, at the freezing-point of benzene, gave a value required for the formula $C_{21}H_{40}$.

1.1020 grams oil and 25.1400 grams benzene gave a depression of 0°.734.

Calculated for $C_{21}H_{40}$.	Found.
292	292.6

The index of refraction found, 1.465, confirmed the same formula:

Calculated for $C_{21}H_{40}$.	Found.
94.56	94.45

Hydrocarbon $C_{22}H_{42}$, B. P. 224°–227° (30 mm.).—After the tenth distillation 22 grams collected at 224°–227°, the sp. gr. of which was 0.8480 at 20°. After filtration at —10° and treatment with acid in gasoline solution, the sp. gr was 0.8614. The percentages of carbon and hydrogen were those required for the series C_nH_{2n-2}.

I. 0.1403 gram oil gave 0.4438 gram CO_2 and 0.1670 gram H_2O.

II. 0.1571 gram oil gave 0.4970 gram CO_2 and 0.1901 gram H_2O.

	Calculated for $C_{22}H_{42}$.	Found. I.	Found. II.
C	86.25	86.27	86.27
H	13.75	13.31	13.53

The molecular weight, determined at the freezing-point of benzene, corresponded to the formula $C_{22}H_{42}$.

0.8385 gram oil and 21.6023 grams benzene gave a depression of 0°.602.

Calculated for $C_{22}H_{42}$.	Found.
306	309

This formula was further confirmed by the molecular weight, determined at the boiling-point of benzene, which gave 310.

The index of refraction, 1.4690, supported the same formula, as shown by the corresponding molecular refraction:

Calculated for $C_{22}H_{42}$.	Found.
99.16	99.60

Hydrocarbon $C_{24}H_{46}$, B. P. 237°–240° (30 mm.).—The hydrocarbon $C_{22}H_{44}$ did not appear in the small amounts of distillates between 227° and 235°. Within the limits 237°–240° (30 mm.), 40 grams collected, which was solid with paraffin at ordinary temperatures. After filtration at —10° the thick, viscous oil gave sp. gr. 0.8639. The percentages of carbon and hydrogen were those required for the series C_nH_{2n-2}.

0.1515 gram oil gave 0.4804 gram CO_2 and 0.1855 gram H_2O.

	Calculated for $C_{24}H_{46}$.	Found.
C	86.23	86.48
H	13.77	13.70

The molecular weight, determined at the freezing-point of benzene, gave the value required for $C_{24}H_{46}$.

1.0900 grams oil and 28.0340 grams benzene gave a depression of 0°.570.

Calculated for $C_{24}H_{46}$.	Found.
334	334

With hydrocarbons of such high molecular weights, the limits of accuracy are reached in determinations by the cryoscopic method with the aid of solvents commonly used, on account of the slight depression of the freeziug-point.

A determination of the index of refraction gave 1.4715, which corresponds to the molecular refraction of $C_{21}H_{42}$.

Calculated for $C_{21}H_{42}$.	Found.
108.4	108

Several higher fractions were collected at points where the oil showed a tendency to accumulate and the results of analysis indicated a series still poorer in hydrogen, C_nH_{2n-4}. Twenty-five grams of the oil collected at 253°–255°, from which the solid was separated by filtration at —10° and the heavy viscous oil was purified by sulphuric acid in gasoline solution ; sp. gr. of the purified oil was 0.8842 at 20°. The values for carbon and hydrogen were those required for the series C_nH_{2n-4}.

0.1424 gram oil gave 0.4511 gram CO_2 and 0.1718 gram H_2O.

	Calculated for $C_{23}H_{42}$.	Found.
C	86.79	86.42
H	13.21	13.49

Several attempts to determine the molecular weight of this hydrocarbon by the freezing-point method failed, on account of the slight depression and the amount of oil was not sufficient for a determination by the boiling-point method. The index of refraction was found to be 1.4797, which corresponds to the following molecular weight:

Calculated for $C_{23}H_{42}$.	Found.
101.7	162.1

A fraction that collected in considerable quantity at 263°–265° (30 mm.), after treatment with sulphuric acid in gasoline solution and filtration at —10°, gave sp. gr. 0.8864 at 20°. The percentages of carbon and hydrogen were as follows:

0.1470 gram oil gave 0.4670 gram CO_2 and 0.1752 gram H_2O.

	Calculated for $C_{23}H_{44}$.	Found.
C	86.75	86.68
H	13.25	13.32

The molecular weight of this hydrocarbon was not determined for the same reasons as the preceding one. A determination of the index of refraction gave 1.4802, corresponding to the molecular refraction :

Calculated for $C_{24}H_{44}$.	Found.
106.5	106.3

A fraction of 40 grams, collected at 275°–278° (30 mm.), was filtered at —10° and the thick viscous oil purified with acid. It gave sp. gr. 0.8912 at 20° and percentages of carbon and hydrogen required for the series C_nH_{2n-4}.

0.1547 gram oil gave 0.4914 gram CO_2 and 0.1814 gram H_2O.

	Calculated for $C_{25}H_{46}$.	Found.
C	86.71	86.66
H	13.29	13.11

The molecular weight of this hydrocarbon was not determined. The index of refraction was found to be 1.4810 and the molecular refraction as follows :

Calculated for $C_{25}H_{46}$.	Found.
110.9	110.5

While the precise formulas of the last three hydrocarbons are not determined with as complete data as those preceding, it is evident that the series C_nH_{2n-4} is established.

Ohio petroleum is, therefore, composed chiefly of the series C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, and C_nH_{2n-4}. It resembles Pennsylvania petroleum in the large proportion of solid paraffin hydrocarbons; but the greater portion of the fractions boiling above 216° consists of the series C_nH_{2n}, which, together with the series poorer in hydrogen, explains the higher specific gravity of the crude oil and distillates prepared from it. It is probable that series still poorer in hydrogen are contained in the less volatile portions that cannot be distilled without decomposition.

The following table gives a summary of the hydrocarbons described in this paper, with their boiling-points and specific gravity at 20° :

Hydrocarbons Separated from Ohio Trenton Limestone Petroleum.

Series.	Formula.	Boiling-point.		Sp. gr. at 20°.
C_nH_{2n}	$C_{12}H_{24}$	211°–213°	atm. pressure	0.7970
"	$C_{13}H_{26}$	223°–225°	" "	0.8055
"	$C_{14}H_{28}$	138°–140°	30 mm.	0.8129
"	$C_{15}H_{30}$	152°–154°	"	0.8204
"	$C_{16}H_{32}$	164°–168°	"	0.8254
"	$C_{17}H_{34}$	177°–179°	"	0.8335
C_nH_{2n-2}	$C_{19}H_{36}$	198°–202°	"	0.8364
"	$C_{21}H_{40}$	213°–217°	"	0.8417
"	$C_{23}H_{42}$	224°–227°	"	0.8614
"	$C_{24}H_{46}$	237°–240°	"	0.8639
C_nH_{2n-4}	$C_{23}H_{42}$	253°–255°	"	0.8842
"	$C_{24}H_{44}$	263°–265°	"	0.8864
"	$C_{25}H_{46}$	275°–278°	"	0.8912

II. THE HYDROCARBONS IN CANADIAN PETROLEUM WITH HIGH BOILING-POINTS.

By Charles F. Mabery.

In a former paper[1] the constituents of Canadian Corniferous limestone petroleum distilling below 216° were described and were shown, by analysis and determination of molecular weights, to belong to the series C_nH_{2n+2}, to the hydrocarbon $C_{11}H_{22}$ boiling at 196°. The hydrocarbon boiling at 216° was found to be $C_{12}H_{24}$. Since several series have appeared in Pennsylvania and Ohio Trenton limestone crude oil, it seemed of interest to ascertain the series which form the main constituents of Canadian petroleum in the portions with high boiling-points. The distillates separated as a part of the former work were available for the study of the higher constituents.[2] Examination of the fraction collected at 216° was repeated and further results were obtained in verification of the former work which assigned the formula $C_{12}H_{24}$ to this hydrocarbon.

A determination of molecular weight established the formula $C_{12}H_{24}$.

0.4528 gram oil and 23.375 grams benzene gave a depression of 0.555.

[1] *Loc. cit.*

[2] A part of this work was performed by Mr. E. T. Numsen, who selected it as the subject of a thesis for the degree of Bachelor of Science.

Calculated for $C_{12}H_{24}$.	Found.
168	171

The chlorine product was formed by the action of chlorine on the hydrocarbon standing over water. On fractionating the product most of it collected at 160° (15 mm.) and this distillate gave sp. gr. 0.9145 at 20°.

The percentage of chlorine corresponded to the formula $C_{12}H_{23}Cl$.

0.1910 gram oil gave 0.1338 gram AgCl.

Calculated for $C_{12}H_{24}$.	Found.
17.52	17.32

The molecular weight of the chlorine product, at the freezing-point of benzene, agreed with the value required by the same formula.

0.361 gram oil and 20.79 grams benzene gave a depression of 0°.425.

Calculated for $C_{12}H_{23}Cl$.	Found.
202.5	200

Distillation of the higher fractions was repeated several times, to collect, so far as possible, the hydrocarbons within narrow limits.

Hydrocarbon $C_{13}H_{26}$, B. P. 228°–230°.—The next fraction examined collected at 228°–230° after the twentieth distillation. Without purification it gave sp. gr. 0.8087 at 20°. After thorough agitation with concentrated and fuming sulphuric acid the sp. gr. was 0.7979, which agrees closely with that of the hydrocarbon $C_{13}H_{26}$ separated from Ohio petroleum.

Analysis gave values required for the series C_nH_{2n}.

0.1614 gram oil gave 0.5068 gram CO_2 and 0.2060 gram H_2O.

	Calculated for $C_{13}H_{26}$.	Found.
C	85.70	85.64
H	14.30	14.28

A determination of the molecular weight gave values required for $C_{13}H_{28}$.

0.4631 gram oil and 17.79 grams benzene gave a depression of 0°.689.

Calculated for $C_{13}H_{28}$.	Found.
182	185

This formula was further verified by determination of its index of refraction, 1.444, which corresponded to the molecular refraction :

Calculated for $C_{13}H_{28}$.	Found.
59.84	60.59

The formula was still further confirmed by its chloride, which was formed by passing chlorine through the purified oil, over water, in diffuse sunlight, until sufficient was absorbed to form the greatest yield of monochloride. After several distillations *in vacuo*, a considerable portion collected at 165° (15 mm.). A Carius determination gave a percentage of chlorine required for the monochloride.

0.1548 gram oil gave 0.1014 gram AgCl.

	Calculated for $C_{13}H_{27}Cl$.	Found.
Cl	16.40	16.20

The molecular weight of the chloride was determined by the freezing-point method.

0.3069 gram oil and 19.14 grams benzene gave a depression of 0°.355.

Calculated for $C_{13}H_{27}Cl$.	Found.
216.5	220.4

The formula was also shown by its index of refraction, 1.465, which corresponded to the molecular refraction :

Calculated for $C_{13}H_{27}Cl$.	Found.
64.78	65.02

The sp. gr. of the chloride found was 0.9221.

Hydrocarbon $C_{14}H_{30}$, *B. P. 141°–143° (50 mm.).*—After the

twentieth distillation a fraction collected, in considerable quantity, within the limits 141°–142° (50. mm.) and gave, without purification, sp. gr. 0.8206 at 20°. After purification with concentrated and fuming sulphuric acid its sp. gr. was 0.8099. This hydrocarbon was shown by analysis to be of the series C_nH_{2n}:

I. 0.1657 gram oil gave 0.5185 gram CO_2 and 0.2135 gram H_2O.

II. 0.1656 gram oil gave 0.5201 gram CO_2 and 0.2079 gram H_2O.

	Calculated for $C_{14}H_{28}$.	Found. I.	Found. II.
C	85.70	85.34	85.65
H	14.30	14.35	14.04

The formula was shown by its molecular weight.

0.3121 gram oil and 18.46 grams benzene gave a depression of 0°.418.

Calculated for $C_{14}H_{28}$.	Found.
196	198

The hydrocarbon gave an index of refraction of 1.449, which corresponded to the molecular refraction of the same formula:

Calculated for $C_{14}H_{28}$.	Found.
64.44	65.02

The hydrocarbon distilled under atmospheric pressure, with some decomposition, at 244°–248°. Further confirmation of the formula was obtained by the composition of the chloride, which was formed in the manner described above. The product of chlorination was fractionally distilled, which caused a considerable portion to collect at 180° (15 mm.); the sp. gr. of the chloride was 0.9288 at 20°. The percentage of chlorine agreed with that required for the monochloride.

0.1690 gram substance gave 0.1039 gram AgCl.

	Calculated for $C_{14}H_{27}Cl$.	Found.
Cl	15.40	15.21

The molecular weight was found at the freezing-point of benzene.

0.7890 gram substance and 23.80 grams benzene gave a depression 0°.718.

Calculated for $C_{14}H_{27}Cl$.	Found.
230.5	226.4

The index of refraction, 1.471, corresponded to the same molecular weight.

Calculated for $C_{14}H_{27}Cl$.	Found.
69.39	69.35

Another fraction of the chlorine product collected in considerable quantity at 197°–200° (15 mm.); after purification, it boiled near to 200° and gave sp. gr. 1.0066 at 20°. The percentage of chlorine indicated a dichloride.

0.1669 gram substance gave 0.1680 gram AgCl.

	Calculated for $C_{14}H_{26}Cl_2$.	Found.
Cl	26.80	24.90

The low percentage of chlorine is doubtless due to incomplete chlorination. The index of refraction found, 1.489, corresponds to the molecular refraction of the dichloride.

Calculated for $C_{14}H_{26}Cl_2$.	Found.
74.33	76.12

Hydrocarbon $C_{18}H_{30}$, B. P. 159°–160° (60 mm.).—As a considerable portion of the distillates collected constant at 159°-160° (50 mm.), after the twentieth distillation, this fraction was selected for the identification of the next hydrocarbon, which proved to be $C_{18}H_{30}$. It gave sp. gr. 0.8311 at 20°, before purification and, after thorough agitation with concentrated and fuming sulphuric acid, 0.8192. Determinations of carbon and hydrogen indicate the series C_nH_{2n}.

0.1586 gram oil gave 0.4961 gram CO_2 and 0.2007 gram H_2O.

	Calculated for $C_{18}H_{30}$.	Found.
C	85.70	85.30
H	14.30	14.16

This formula was indicated by the molecular weight determined at the freezing-point of benzene.

0.3634 gram oil and 19.276 grams benzene gave a depression of 0°.443.

Calculated for $C_{15}H_{30}$.	Found.
210	208

This formula was confirmed by the molecular refraction, calculated from the index found, 1.452.

Calculated for $C_{15}H_{30}$.	Found.
69.04	69.15

A portion of the hydrocarbon was chlorinated and the product distilled until it came together in large amount at 190° (15 mm.); its sp. gr. was 0.9358 at 20°. Determinations of chlorine established its composition.

I. 0.1579 gram substance gave 0.0951 gram AgCl.
II. 0.2032 gram substance gave 0.1158 gram AgCl.

	Calculated for $C_{15}H_{29}Cl$.	Found. I.	Found. II.
Cl	14.45	14.55	14.09

For further identification the molecular weight was ascertained.

0.4520 gram substance and 17.44 grams benzene gave a depression of 0°.529.

Calculated for $C_{15}H_{29}Cl$.	Found.
244.5	240

The index of refraction found, 1.455, corresponded to a molecular refraction of the same formula:

Calculated for $C_{15}H_{29}Cl$.	Found.
73.99	74.83

It would have been interesting to include in this examination the hydrocarbons with still higher boiling-points, to ascertain where the series C_nH_{2n-2} and C_nH_{2n-4} begin, for comparison with the corresponding distillates from other petroleum; but the work described above exhausted the supply of dis-

tillates prepared from the large distillation of crude oil and the great amount of labor involved in working up to the well distilled fractions from the crude oil, prevented a repetition, on account of the attention demanded by more important lines of work.

The hydrocarbons described above, representing a considerable proportion of Canadian petroleum, correspond, in boiling-points and in composition, to those separated from Ohio Trenton limestone petroleum. An explanation of the higher specific gravity of Canadian crude oil and commercial products obtained from it, as compared with Ohio, Pennsylvania, West Virginia, Kentucky and similar crude oils, is given by the larger proportion, in the Canadian oil, of the series C_nH_{2n} and series poorer in hydrogen. In the Canadian crude oil this series begins in the fraction 196°, a temperature much lower than that at which it is found in any of the other petroleums mentioned and, no doubt, it forms a much larger proportion of the crude oil. The same is doubtless true of the series still poorer in hydrogen. As shown in a former paper, the series C_nH_{2n} does not appear in Pennsylvania petroleum until the hydrocarbon $C_{11}H_{24}$ is reached; but in Pennsylvania petroleum the first hydrocarbon of this series is $C_{11}H_{22}$. In Ohio petroleum the series begins with the hydrocarbon $C_{13}H_{24}$.

Doubtless the changes in series in the crude oil are more gradual than appears from our results. One distillation, as conducted in a refinery, affords only a partial separation, but in long-continued fractionations the tendency toward collection "in heaps" indicates an accumulation of the hydrocarbons in the vicinity of their boiling-points. The smaller quantities which collect between are composed of mixtures of higher and lower boiling hydrocarbons; doubtless the larger portion is not entirely free from higher and lower boiling constituents. Perhaps this causes a balancing of molecular weights, but it is evident that the contaminating higher and lower bodies are not sufficient in amounts to interfere with determinations that establish the formula of the principal hydrocarbon.

The following table gives the hydrocarbons separated from

Canadian petroleum and the chlorides prepared from them, with their boiling-point and specific gravity :

	Formula.	Boiling-point.		Sp. gr. at 20°.
Hydrocarbon	$C_{12}H_{24}$	216°		
Chloride	$C_{12}H_{23}Cl$	160°	15 mm.	0.9145
Hydrocarbon	$C_{13}H_{26}$	228°–230°	" "	0.8087
Chloride	$C_{13}H_{25}Cl$	165°	" "	0.9221
Hydrocarbon	$C_{14}H_{28}$	141°–143°	50 "	0.8096
Chloride	$C_{14}H_{27}Cl$	180°	15 "	0.9288
Hydrocarbon	$C_{15}H_{30}$	159°–169°	50 "	0.8192
Chloride	$C_{15}H_{29}Cl$	190°	15 "	0.9358

III. HYDROCARBONS IN SANTA BARBARA CRUDE OIL.

Composition of California Petroleum (Continued).

In a paper[1] published two years ago, allusion was made to a specimen of peculiar heavy petroleum that had been received from Mr. J. B. Bardwell, Summerland, Santa Barbara County, Cal., representing the heavy oil that is taken from wells sunk below the Pacific Ocean. An examination of this petroleum seemed desirable, especially because it is the heaviest specimen, with one exception, that has been examined in this laboratory. It represents the last member of a series beginning with the light-yellow Berea Grit oil from Southern Ohio, which was found by Mabery and O. C. Dunn[2] to be the lightest petroleum that had come to our knowledge.

This work was undertaken by Mr. C. V. Zoul.[3] The oil, as it was received, had the consistency of heavy tar ; it would scarcely flow at ordinary temperatures.

Its sp. gr. was 0.9845 at 20° ; it contained 0.84 per cent sulphur, 1.25 per cent nitrogen, 86.32 per cent carbon and 11.70 per cent hydrogen, showing that the crude oil is composed, at least to a large extent, of hydrocarbons poorer in hydrogen than petroleum from most other sources. In attempting to ascertain the composition of this petroleum, 2,000 grams were fractionated under 60 mm., collecting within 5°. The first distillate came over at 200° (atmospheric pressure) and only small amounts were collected below 175° (60 mm.). The distillation was car-

[1] P. Am. Acad., 36, 255.
[2] This Journal, 18, 1 (1896).
[3] The subject of a thesis for the degree of Bachelor of Science.

ried to 365°, without attempting to collect closer than in 5° fractions, because the principal object was to ascertain the form of the hydrocarbons, although, as will appear, the fractions gave fairly close values for their molecular weights.

The heavy character of the constituents of this petroleum is shown by the specific gravity of several distillates after the fifth distillation.

150°-155°.	305°-310°.	325°-330°.	240°-245°.
0.8649	0.9641	0.9739	0.9778

The residue at 365° from 2,000 grams was 200 grams, which showed that the greater portion of the oil distilled between 150° and 360°, or within a range of about 200°. Only 85 grams came over below 150° (60 mm.); at higher temperatures the fractions collected in larger amounts at certain points and these distillates were selected to ascertain the series of hydrocarbons:

	155°-160°.	175°-180°.	195°-200°.	210°-215°.
Weights	25	70	50	75
	223°-230°.	250°-255°.	310°-315°.	340°-345°.
Weights	75	50	80	45

Hydrocarbon $C_{12}H_{24}$, B. P. 150°–155° (60 mm.).—Before treatment with acids, the distillate 150°–155° gave sp. gr. 0.8649 at 20° and 0.8621 after purification with concentrated and fuming sulphuric acid and sodium hydroxide.

The percentages of carbon and hydrogen corresponded to the formula $C_{12}H_{24}$.

0.1357 gram oil gave 0.4312 gram CO_2 and 0.1653 gram H_2O.

	Calculated for $C_{12}H_{24}$.	Found.
C	86.67	86.68
H	13.33	13.62

The molecular weight of this hydrocarbon, at the freezing-point of benzene, indicated the same formula.

0.3641 gram oil and 18.17 grams benzene gave a depression of 0°.541.

Calculated for $C_{13}H_{24}$.	Found.
180	181.5

A determination of the index of refraction gave 1.4681, from which the molecular refraction was calculated:

Calculated for $C_{13}H_{24}$.	Found.
57.74	58.05

Hydrocarbon $C_{16}H_{30}$, B. P. 175°–180° (60 mm.).—The fraction 175°–180° was rather thick and viscous, with sp. gr. 0.8832 at 20°; after purification it had practically the same, 0.8808. Percentages of carbon and hydrogen corresponded to the formula $C_{16}H_{30}$.

0.1533 gram oil gave 0.4879 gram CO_2 and 0.1797 gram H_2O.

	Calculated for $C_{16}H_{30}$.	Found.
C	86.48	86.82
H	13.52	13.11

A determination of molecular weight, at the freezing-point of benzene, gave the same formula.

0.7134 gram oil and 16.56 grams benzene gave a depression of 0°.974.

Calculated for $C_{16}H_{30}$.	Found.
222	216.7

The index of refraction was found to be 1.470, which gave the molecular refraction for the formula $C_{16}H_{30}$.

Calculated for $C_{17}H_{30}$.	Found.
71.6	70.3

Hydrocarbon $C_{17}H_{30}$, B. P. 190°–195° (60 mm.).—Very little difference in specific gravity of this distillate was found before and after purification. The values were 0.8969 and 0.8919, respectively. The proportions of carbon and hydrogen indicated a change in series from C_nH_{2n-2} in the preceding hydrocarbons to C_nH_{2n-4}.

0.1444 gram oil gave 0.4628 gram CO_2 and 0.1664 gram H_2O.

	Calculated for $C_{17}H_{30}$.	Found.
C	87.18	87.40
H	12.82	12.90

Determination of the molecular weight, at the freezing-point of benzene, gave a value for the formula $C_{17}H_{30}$.

0.8220 gram oil and 18.20 grams benzene gave a depression of 0°.921.

Calculated for $C_{17}H_{30}$.	Found.
234	240

The index of refraction was found to be 1.4778, corresponding to the molecular refraction :

Calculated for $C_{17}H_{30}$.	Found.
74.03	74.27

Hydrocarbon $C_{18}H_{32}$, B. P. 210°–215° (60 mm.).—The viscous distillate 210°–215° gave sp. gr. 0.9085; after thorough treatment with concentrated and fuming sulphuric acid in gasoline solution, the value was 0.8996. The carbon and hydrogen percentages agreed with the series C_nH_{2n-4}.

0.1494 gram oil gave 0.4787 gram CO_2 and 0.1713 gram H_2O.

	Calculated for $C_{18}H_{32}$.	Found.
C	87.10	87.38
H	12.90	12.83

An 18-carbon compound was shown by a determination of its molecular weight, at the freezing-point of benzene.

0.8281 gram oil and 18.94 grams benzene gave a depression of 0°.864.

Calculated for $C_{18}H_{32}$.	Found.
248	248

The index of refraction was found to be 1.484 at 20° and the molecular refraction :

Calculated for $C_{18}H_{32}$.	Found.
78.64	78.86

Hydrocarbon $C_{24}H_{44}$, B. P. 250°–255° (60 mm.).—The viscous distillate 250°–255° gave sp. gr. 0.9299 at 20°, and carbon and hydrogen percentages for the series C_nH_{2n-4}.

0.1481 gram oil gave 0.4745 gram CO_2 and 0.1628 gram H_2O.

	Calculated for $C_{24}H_{44}$.	Found.
C	87.42	87.40
H	12.58	12.29

Determinations of the molecular weight, at the freezing-point of naphthalene, gave results corresponding to the formula $C_{24}H_{44}$.

I. 0.5682 gram oil and 11.66 grams naphthalene gave a depression of 1°.022.

II. 0.4777 gram oil and 12.21 grams naphthalene gave a depression of 0°.819.

Calculated for $C_{24}H_{44}$.	Found. I.	Found. II.
332	329	330

Hydrocarbon $C_{27}H_{48}$, B. P. 310°–315° (60 mm.).—This distillate was very thick and viscous. For purification it was dissolved in light gasoline; after treatment the gasoline was distilled in a current of carbon dioxide. The original distillate gave sp. gr. 0.9548, which, by treatment with acid, became 0.9451, with practically no change.

The carbon and hydrogen had values required for the series C_nH_{2n-8}.

I. 0.1479 gram oil gave 0.4757 gram CO_2 and 0.1588 gram H_2O.

II. 0.1486 gram oil gave 0.4769 gram CO_2 and 0.1613 gram H_2O.

	Calculated for $C_{27}H_{48}$.	Found. I.	Found. II.
C	87.59	87.72	87.52
H	12.41	12.00	12.13

A determination of its molecular weight, at the freezing-point of benzene, gave a value required for a 27-carbon compound.

0.3985 gram oil and 17.488 grams benzene gave a depression of 0°.300.

Calculated for $C_{27}H_{48}$.	Found.
370	372

This formula was supported by the index of refraction, 1.5146, from which the molecular refraction was calculated.

Calculated for $C_{27}H_{46}$.	Found.
116	118

Hydrocarbon $C_{29}H_{50}$, B. P. 340°-345° (60 mm.).—This distillate was purified as before in light gasoline. After the gasoline was removed there remained an extremely viscous, light-yellow oil, that would scarcely flow at ordinary temperatures; sp. gr. 0.9778 at 20°. The original fraction had scarcely any odor, consequently contained no phenol derivative.

The purified oil gave the following values for carbon and hydrogen:

0.1489 gram oil gave 0.4781 gram CO_2 and 0.1634 gram H_2O.

	Calculated for $C_{29}H_{50}$.	Found.
C	87.44	87.76
H	12.56	12.28

The higher distillates were not examined, because the results described above are sufficient to establish the composition of the main body of the crude oil. The difficulties in separating hydrocarbons at these high temperatures at all well-fractioned and of obtaining analytical values to decide their composition, are very great. It is evident that the series of hydrocarbons which compose Santa Barbara petroleum, explains the peculiar nature of the oil, which is unlike any other that has been examined in this laboratory. The most volatile distillates are composed of the series C_nH_{2n-2}, and the proportion of hydrogen gradually falls off through the series C_nH_{2n-4} and C_nH_{2n-8}. This change is accompanied by a corresponding increase in specific gravity. These viscous hydrocarbons evidently approach the constituents of the asphaltic oils and natural tars. It is easy to see how petroleum is converted, by slow evaporation under natural conditions, into the great beds of tars and asphalts and this affords the most probable explanation of their formation.

The hydrocarbons described in this paper, with their boiling-point and specific gravity, are brought together in the following table:

Hydrocarbons Separated from Santa Barbara (Cal.) Petroleum.

	Formula.	Boiling-point.	Sp. gr. at 20°.
Hydrocarbon	$C_{13}H_{34}$	150°–155°, 60 mm.	0.8621
"	$C_{16}H_{30}$	175°–180°, "	0.8808
"	$C_{17}H_{30}$	190°–195°, "	0.8919
"	$C_{18}H_{32}$	210°–215°, "	0.8996
"	$C_{24}H_{44}$	250°–255°, "	0.9299
"	$C_{27}H_{46}$	310°–315°, "	0.9451
"	$C_{29}H_{50}$	340°–345°, "	0.9778

IV. SEPARATION OF SOLID PARAFFIN HYDROCARBONS FROM PETROLEUM WITHOUT DISTILLATION.

By Charles F. Mabery and Otto J. Sieplein.

By the method of distillation, which is the only means for the separation of the petroleum hydrocarbons, it is not possible to determine whether the solid paraffin hydrocarbons are contained in the crude oil or whether they may not be formed by decomposition.

As a direct proof that the solid hydrocarbons are actually contained in petroleum we have separated them without distillation. Three kilos of an average specimen of Pennsylvania crude petroleum were allowed to stand in a shallow pan, exposed to a current of air, in a strong flue draft, for thirty days. The change was shown by the increase in specific gravity:

Sp. gr. at 15° before exposure.		
Dec. 9.	Dec. 12.	Jan. 8.
0.815	0.840	0.862

When taken from the flue, January 8th, the residue weighed 1 kilo, which showed a loss of 66.67 per cent. The original oil distilled as follows:

50°-150°.	150°-200°.	200°-250°.	250°-300°.	+300°.
21 per cent	11 per cent	11 per cent	13 per cent	42 per cent

The residue above 300° is, therefore, about the same in weight as the residue left by evaporation. That the loss by evaporation had practically ceased at the end of one month was shown by allowing the residue to stand one year in the same place, exposed to draft as before, but there was no change in weight nor in specific gravity.

Combustion of the crude oil:

0.1968 gram oil gave 0.4915 gram CO_2 and 0.2512 gram H_2O.

C	85.51
H	14.18

Combustion of the residue after thirty days' evaporation:

0.1559 gram oil gave 0.4925 gram CO_2 and 0.1559 gram H_2O.

C	86.16
H	13.69

Evaporation of the portions with lower boiling-points, which form the greater part of the series C_nH_{2n+2}, leaves a larger proportion or series poorer in hydrogen, C_nH_{2n} and C_nH_{2n-2}, corresponding to the composition shown by analyses.

On cooling with ice the residue from evaporation became quite solid.

On distillation, 28 per cent came over below 30°, 6 per cent at 300°–360°, with a residue above 360° of 66 per cent.

The amount of solid hydrocarbons in the residue was determined by the method suggested by Zaliozieckí. Fifty grams of the residue with fused oil, mostly isoamyl alcohol, was allowed to stand at 0° for 24 hours; 250 grams alcohol were then added and the precipitate collected on a filter and washed with a mixture of fusel oil and alcohol. The precipitate on the filter-paper was then placed in an extraction apparatus and extracted with benzene. After evaporation of the benzene the residue was heated to 140° for 1 hour to remove the last traces of fusel oil. Nineteen and eight-tenths grams of a greenish-black solid remained, melting at 32°, equivalent to 39.6 per cent of the heavy residue, or to 14 per cent of the original oil, before evaporation.

The solid was again dissolved in fusel oil and precipitated by alcohol, giving a smaller quantity melting at 45°. This treatment, repeated, gave a light-brown substance melting at 57°, which was then dissolved in ether and precipitated by alcohol; this product had less color and another treatment gave a white solid melting at 61°. Its sp. gr. was 0.7966 at

70°, corresponding to that of paraffin and it gave percentages of carbon and hydrogen required for paraffin hydrocarbons.

0.1511 gram substance gave 0.4730 gram CO_2 and 0.1984 gram H_2O.

C	85.37
H	14.69

The specific gravity, melting-point and composition of this substance indicate that it was composed of paraffin hydrocarbons and demonstrated the presence of solid paraffin hydrocarbons in Pennsylvania petroleum.

Paraffin collected from heavy distillates in the refinery is, therefore, obtained as it exists in the original crude oil and is not formed during distillation. Indeed, as explained in another paper, it cannot be formed, for any decomposition of petroleum hydrocarbons by heat removes hydrogen, with a conversion of the hydrocarbon substances into a lower series; for example, of the paraffin hydrocarbons of the series C_nH_{2n+2} into the series C_nH_{2n}, C_nH_{2n-2}, etc. and, perhaps, also forming methylenes and condensed methylenes. Such changes do not involve an absorption of oxygen into the hydrocarbon molecule, but a removal of hydrogen, by oxygen, as water. That oxygen compounds of the nature of phenols are found in petroleum from various fields has been fully demonstrated independently by Richardson and by Mabery (data not published) and it is quite probable that most petroleums contain these bodies to a greater or less extent; but they have been formed by natural processes.

In ordinary refinery distillation there is probably little decomposition below 300°, but at this point "cracking" begins and increases rapidly to the end. There are, doubtless, reactions at higher temperatures between nitrogen, sulphur and oxygen compounds. Then the breaking down in series begins, with loss of hydrogen, through the asphaltic hydrocarbons, until finally coke is reached, which forms a considerable proportion of the products of refining.

V. THE SOLID PARAFFIN HYDROCARBONS THAT COLLECT IN CERTAIN OIL WELLS IN PENNSYLVANIA.

In attempting to determine the series of hydrocarbons and

members of the series that form the solid constituents of Pennsylvania petroleum, it seemed of interest to examine the semi-solid product that collects in considerable quantities in some of the Pennsylvania wells, especially at Coreopolis, Pa. The Petrolatum Co. collects large quantities of this pasty substance from their wells and from it manufactures various preparations, such as vaseline and cosmoline. The crude product is obtained in the form of a light-yellow, pasty mass, from which it is impossible to separate a solid by pressure in filter-paper or by filtration. It evidently consists of an emulsion of the high-boiling oils with the solid hydrocarbons, which, no doubt, are in part dissolved in the oily constituents.

Having obtained several gallons of this substance through the kindness of the Coreopolis Petrolatum Company in October, 1898, I undertook an examination of it with the principal object of proving the presence of solid hydrocarbons and identifying their composition, as to series and molecular formulas, for comparison with the solid hydrocarbons which I have separated from Pennsylvania crude oil and from commercial paraffin. These semi-solid emulsions have, no doubt, been formed by evaporation of the lighter constituents of petroleum and the solid hydrocarbons are, therefore, what were contained in the original petroleum. An opportunity was also afforded to confirm the presence of the solid constituents of paraffin in crude petroleum, a question concerning which a doubt is often expressed by refiners.

The specimen was received in the form of a thick paste, with sp. gr. 0.8345 at 60°. In beginning the distillation 9380 grams were distilled in a porcelain still, under 50 mm. pressure and the distillates collected in the following quantities :

	-195°.	195°-200°.	200°-245°.	245°-265°.	265°-285°.
Grams	905	865	895	850	830
	285°-315°.	315°-330°.	330°-342°.		Residue.
Grams	200	790	885		3000

Distillation of these fractions was continued within 10°, 5° and 2° until, after the sixth distillation, larger quantities collected at the following temperatures :

242°–244° 268°–270° 280°–282° 308°–310° 328°–330°
340°–342° 352°–354° 368°–370° 382°–384°

Because the distillates below 268° showed, by their thin pasty condition, that they contained only small proportion of solid hydrocarbon, no attempts were made to separate their constituents. The fraction 272°–274° gave sp. gr. 0.8116 at 20° and the following percentages of carbon and hydrogen :

0.1600 gram substance gave 0.5058 gram CO_2 and 0.1963 gram H_2O.

Calculated for $C_{22}H_{46}$.	Found.
86.21	86.22
13.79	13.73

This fraction, therefore, consisted mainly of a hydrocarbon of the series C_nH_{2n-2}, and the same will appear in the higher fractions to be described.

On cooling the distillates with salt and ice and attempting to separate the solid by filtration under pressure, the emulsion was so complete that scarcely any of it remained on the filter ; but such a wide difference was observed in the solubility in ether and alcohol, between the crystalline and amorphous solid, that it afforded an easy means of separation.

The distillate 272°–274° (30 mm.) was, therefore, dissolved in a suitable mixture of ether and alcohol, cooled with salt and ice and filtered cold. The solid collected was pressed and the crystallization repeated, which gave a perfectly white crystalline hydrocarbon melting at 50°–51°, giving sp. gr. 0.7900 at 60° and carbon and hydrogen indicating the series C_nH_{2n+2}.

0.1516 gram substance gave 0.4728 gram CO_2 and 0.1973 gram H_2O.

	Calculated for tetracosane, $C_{24}H_{50}$.	Found.
C	85.21	85.06
H	14.79	14.56

The quantity of the solid hydrocarbon obtained was small, evidently not sufficient to influence the proportions of carbon and hydrogen in the unfiltered distillate. Although the amount obtained was not enough for a determination of its

molecular weight, its melting-point and specific gravity, identical with those of the hydrocarbon tetracosane separated from the paraffin distillate 272°–274°, indicate that it has the same composition.

Tetracosane, obtained by Krafft[1] by reduction of the ketone derived from barium stearate and barium heptylate, melted at 51°, but the specific gravity of Krafft's hydrocarbon was somewhat lower than that of the hydrocarbon from petroleum.

The quantities of the distillates between 274° and 316° were too small to permit of a separation of crystalline hydrocarbons in sufficient amounts for identification of individual constituents.

The pasty solid collected at 316°–318° (50 mm.) yielded a solid hydrocarbon, by crystallization from alcohol and ether, that melted at 66°. The crude distillate gave sp. gr. 0.8212 at 20°.

0.1564 gram substance gave 0.4935 gram CO_2 and 0.1939 gram H_2O.

	Calculated for hentricontane, $C_{31}H_{64}$.	Found.
C	86.15	86.05
H	13.85	13.80

The purified solid gave sp. gr. 0.7997 at 70° and carbon and hydrogen required for the series C_nH_{2n+2}.

0.1499 gram substance gave 0.4698 gram CO_2 and 0.1969 gram H_2O.

	Calculated for $C_{21}H_{44}$.	Found.
C	85.31	85.45
H	14.69	14.69

The formula of this hydrocarbon was further verified by its molecular weight.

0.3648 gram substance and 12.12 grams naphthalene gave a depression of 0°.471.

Calculated for $C_{21}H_{44}$.	Found.
436	441

[1] Ber. d. chem. Ges., 15, 1718 (1882).

From the ketone palmiton, $C_{31}H_{62}O$, Krafft[1] prepared hentricontane, $C_{31}H_{64}$, m. p. 68°.1, which differs but slightly from that of the hydrocarbon separated from petroleum, 66°.

Because the solid hydrocarbon formed such a small proportion of the original distillate that it did not affect materially the composition of the latter, it evidently could not be compared with the hydrocarbon separated from the corresponding distillate from paraffin, nor with that from crude Pennsylvania petroleum, for the predominating constituents should materiallly affect the boiling-points of all the minor solid ones. This is shown to be true by the high molecular weights and high melting-points of the hydrocarbons separated from Coreopolis distillates, so far as they could be determined. The distillate collected at 328°–330° (50 mm.), after filtration from the solid, had sp. gr. 0.8235 at 70°; after crystallization from ether and alcohol the white solid had sp. gr. 0.7982 at 70°. The proportions of carbon and hydrogen agreed with the formula of the series C_nH_{2n+2}.

The original distillate gave sp. gr. 0.8217. Analysis:

0.1586 gram substance gave 0.4995 gram CO_2 and 0.1925 gram H_2O.

	Calculated for $C_{29}H_{60}$.	Found.
C	86.14	85.86
H	13.86	13.57

The solid, purified by means of ether and alcohol, gave proportions of carbon and hydrogen corresponding to the series C_nH_{2n+2}.

0.1549 gram solid gave 0.4842 gram CO_2 and 0.2075 gram H_2O.

	Calculated for $C_{28}H_{58}$.	Found.
C	85.33	85.25
H	14.67	14.98

The melting-point of the crystalline hydrocarbon was 67°–68°; its molecular weight, at the boiling-point of benzene and also at the freezing-point of naphthalene, indicated the next higher homologue, $C_{32}H_{66}$, dotricontane, but the small quantity

[1] Ber. d. chem. Ges., **15**, 1714.

of substance available for this determination was not sufficient to yield satisfactory results.

The specific gravity of the unpurified distillate 342°–344° (50 mm.) was 0.8288 ; after separation of the solid by freezing and purification by crystallization from ether and alcohol, its sp. gr. was 0.8005 at 75° and it melted at 68°–70°. The unpurified distillate gave carbon and hydrogen corresponding to the series C_nH_{2n-2}.

0.1517 gram substance gave 0.4784 gram CO_2 and 0.1850 gram H_2O.

	Calculated for $C_{20}H_{38}$.	Found.
C	86.12	86.06
H	13.88	13.64

The purified solid gave proportions of carbon and hydrogen required for the series C_nH_{2n+2}.

0.1544 gram solid gave 0.4816 gram CO_2 and 0.2060 gram H_2O.

	Calculated for $C_{22}H_{66}$.	Found.
C	85.33	85.06
H	14.67	14.92

The molecular weight, determined by the boiling-point method, confirmed the formula $C_{32}H_{66}$.

0.5127 gram substance and 12.23 grams benzene gave a depression of 0°.654.

Calculated for $C_{32}H_{66}$.	Found.
438	442

As mentioned above, the solid hydrocarbons form a small proportion of the original oil ; the small amounts that collect at 328°–330° and 340°–342° have, doubtless, nearly the same composition, $C_{32}H_{66}$.

The distillate 366°–368° (50 mm.), before treatment, had sp. gr. 0.8312 ; the solid hydrocarbon separated by freezing, filtration and crystallization from ether and alcohol, had sp. gr. 0.8009 at 80° and melted at 71°–72°. The carbon and hydrogen in the unpurified distillate corresponded to the formula C_nH_{2n-2}.

0.1485 gram substance gave 0.4982 gram CO_2 and 0.1851 gram H_2O.

	Calculated for $C_{31}H_{60}$.	Found.
C	86.11	85.96
H	13.89	13.94

The solid separated from the fraction 366°–368°, after purification, gave 85.41 per cent carbon and 14.74 per cent hydrogen, corresponding to the series C_nH_{2n+2}; it was present in only small quantity and probably differed but slightly from the hydrocarbon contained in the fraction 342°–344°.

The close agreement to the series C_nH_{2n-2}, in the composition of the untreated distillate, before removing the solid hydrocarbon, is due, as explained above, to the very small proportion of the latter, which is C_nH_{2n+2}. The oils separated by filtration are evidently composed, for the greater part, of the series C_nH_{2n-2}, although the low percentage of hydrogen may indicate the presence, in small amounts, of a series even poorer in hydrogen.

The untreated distillate 380°–384° (50 mm.) gave sp. gr. 0.8336, and the solid hydrocarbon obtained by freezing, filtration and crystallization from ether and alcohol, 0.8052 at 80°. It melted at 76°. Determinations of carbon and hydrogen indicated the series C_nH_{2n-2}.

0.1560 gram substance gave 0.4898 gram CO_2 and 0.1943 gram H_2O.

	Calculated for $C_{34}H_{66}$.	Found.
C	86.08	95.82
H	13.92	13.93

The purified solid contained carbon and hydrogen required for the series C_nH_{2n+2}.

0.1501 gram solid gave 0.4695 gram CO_2 and 0.1974 gram H_2O.

	Calculated for $C_{25}H_{72}$.	Found.
C	85.37	85.33
H	14.63	14.71

The molecular weight of the solid, by the boiling-point method, corresponded to the same formula.

1.0012 gram substance and 24.72 grams benzene gave a rise of 0°.212.

Calculated for $C_{35}H_{72}$.	Found.
492	490

As the molecular weights of the hydrocarbons of these series increase, the determinations become more and more difficult and uncertain. The values obtained, together with the other data, support the formulas given. With the high-boiling liquids there is less trouble than with solids.

As formerly explained, the freezing-point of benzene cannot be relied on for solid hydrocarbons with molecular weights much above $C_{20}H_{42}$. At its boiling-point, benzene can be depended on for a somewhat higher range, but becomes uncertain with hydrocarbons in the vicinity of $C_{30}H_{62}$. Other solvents are equally uncertain on account of a lack of solubility or variable influence of the dissolved substance on the freezing-point. After long trial with naphthalene, which promised reliable results on account of its free solvent power and large depression, we found that the substances which had melting-points not far removed from that of naphthalene gave variations in depression too great for reliable calculations of molecular weights.

Solid Hydrocarbons in Pennsylvania Oil Wells.

	Formula.	Melting-point.	Specific gravity.
Tetracosane	$C_{24}H_{50}$	50°–51°	0.7900 at 60°
Hentricontane	$C_{31}H_{64}$	66°	0.7997 at 70°
Dotricontane	$C_{32}H_{66}$	67°–68°	0.8005 at 75°
Tetratricontane	$C_{34}H_{66}$	71°–72°	0.8009 at 80°
Pentatricontane	$C_{35}H_{72}$	76°	0.8052 at 80°

Hydrocarbons of the series C_nH_{2n+2} have now been identified in Pennsylvania petroleum in continuous series, with but few members wanting, from butane, C_4H_{10}, b. p. —10°, to pentatricontane, $C_{35}H_{72}$, b. p. 380°–384°, 50 mm.

VI. COMPOSITION OF COMMERCIAL PARAFFIN.[1]

It has been questionable, even with refiners of petroleum of

[1] A part of the work described in this paper was performed by Mr. H. R. Payne, and formed the subject of a thesis for the degree of Bachelor of Science.

long experience, as to whether paraffin is actually present in the crude oil or whether it is a result of change during the process of refining. It therefore seemed of interest to ascertain whether the hydrocarbons, of which commercial paraffin is composed, are identical with the solid constituents of the crude oils that yield paraffin.

The method of distillation was the same as that employed in distilling the crude oil, except that it was found necessary to pack the neck of the flask with a thick coating of asbestos. With exclusion of air it was found that paraffin could be distilled definitely with no decomposition, but introduction of air, either by leaks or by accident, caused serious decomposition, as shown by the dark color and disagreeable odor of the distillates.

Fifteen hundred grams of the best commercial paraffin was distilled under 40 mm. and the distillates collected at first within 10°, then 5° and finally within 2°, altogether seven times. The lowest distillate collected below 250° and the final residue, above 350°, was only 30 grams. All the distillates were colorless, except the residue, which was slightly brown and nearly odorless. The distillates collected in larger quantities at temperatures corresponding to the boiling-points of hydrocarbons separated from the crude oil as follows:

	Grams.		Grams.
256°–258°	90	316°–318°	35
272°–274°	45	332°–334°	20
282°–284°	70	346°–348°	40
292°–294°	30		

Tricosane $C_{23}H_{48}$, *B. P. 256°–258° (40 mm.).*—The distillate 256°–258°, without purification, melted at 48° and this was not raised by crystallization from alcohol and ether. Tricosane obtained by Krafft[1] melted at 47°.7. Its sp. gr. was determined above its melting-point:

60°	0.7836	70°	0.7814	80°	0.7807

The sp. gr. of tricosane from petroleum differs materially from that of the hydrocarbon which Krafft obtained from the ketone, laurone:

[1] Ber. d. chem. Ges., **15**, 1713 (1882).

47°.7	0.7785	80°.8	0.7570	88°.8	0.7456

Carbon and hydrogen were in proportions required for the series C_nH_{2n+2}.

0.1510 gram substance gave 0.4710 gram CO_2 and 0.1989 gram H_2O.

	Calculated for $C_{23}H_{48}$.	Found.
C	85.20	85.06
H	14.80	14.73

A determination of its molecular weight, at the boiling-point of benzene, gave a value required for tricosane.

0.8907 gram solid and 24.24 grams benzene gave a rise of 0°.295.

Calculated for $C_{23}H_{48}$.	Found.
324	319

Tetracosane $C_{24}H_{50}$, *B. P. 272°–274° (40 mm.)*.—This distillate melted, without purification, at 50°–51° and was not changed by crystallization from alcohol and ether. Krafft's tetracosane, obtained from the ketone derived from barium stearate and barium heptylate, melted at 51°.1. The quantity of tetracosane obtained was not sufficient to determine its specific gravity.

This hydrocarbon was shown, by analysis, to belong to the series C_nH_{2n+2}:

I. 0.1424 gram substance gave 0.4451 gram CO_2 and 0.1923 gram H_2O.

II. 0.1460 gram substance gave 0.4551 gram CO_2 and 0.1955 gram H_2O.

III. 0.1443 gram substance gave 0.4502 gram CO_2 and 0.1924 gram H_2O.

	Calculated for $C_{24}H_{50}$.	Found. I.	Found. II.	Found. III.
C	85.21	85.25	85.00	85.08
H	14.79	14.96	14.97	14.91

The formula was verified by a determination of its molecular weight.

3.0316 gram oil and 22.42 grams benzene gave a rise of 1°.034.

Calculated for $C_{24}H_{50}$.	Found.
338	335

Pentacosane $C_{25}H_{52}$, *B. P. 282°–284° (40 mm.).*—The melting-point of the unpurified distillate, 282°–284°, was 53°–54°; after crystallization from ether and alcohol it melted at 54°. Its sp. gr. was determined above its melting-point.

60°	0.7911	80°	0.7870
70°	0.7881	90°	0.7854

Analysis:

0.1467 gram substance gave 0.4578 gram CO_2 and 0.1950 gram H_2O.

	Calculated for $C_{25}H_{52}$.	Found.
C	85.23	85.09
H	14.77	14.88

The formula was confirmed by a determination of its molecular weight.

1.4324 grams substance and 8.5282 grams benzene gave a rise of 1°.265.

Calculated for $C_{25}H_{52}$.	Found.
352	354

Hexacosane $C_{26}H_{54}$, *B. P. 294°–296° (40 mm.).*—After the seventh distillation, 25 grams, collected at 294°–296°, melted at 55°–56° and was not changed by crystallization from ether and alcohol. Its sp. gr. above its melting-point was:

60°	0.7938	80°	0.7893
70°	0.7918	90°	0.7879

The carbon and hydrogen corresponded to the series C_nH_{2n+2}.

0.1526 gram solid gave 0.4757 gram CO_2 and 0.2027 gram H_2O.

	Calculated for $C_{26}H_{54}$.	Found.
C	85.23	85.02
H	14.77	14.86

Its molecular weight, found at the boiling-point of benzene, verified the formula.

1.6742 grams substance and 13.151 grams benzene gave a rise of 0°.93.

Calculated for $C_{26}H_{54}$.	Found.
366	365

Octocosane $C_{28}H_{58}$, *B. P. 316°–318° (40 mm.).*—At 316°–318° 35 grams collected after the seventh distillation with m. p. 60° which was not changed by crystallization from ether and alcohol. The carbon and hydrogen indicated the series C_nH_{2n+2}.

0.1586 gram oil gave 0.4954 gram CO_2 and 0.2122 gram H_2O.

	Calculated for $C_{28}H_{58}$.	Found.
C	85.28	85.17
H	14.72	14.96

A determination of its molecular weight corresponded to the formula $C_{28}H_{58}$.

I. 1.3337 grams solid and 23.73 grams benzene gave a rise of 0°.362.

II. 1.7964 grams solid and 21.96 grams benzene gave a rise of 0°.53.

Calculated for $C_{28}H_{58}$.	Found.	
	I.	II.
394	397	396

Nonocosane $C_{29}H_{60}$, *B. P. 346°–348° (40 mm.).*—At 346°–348° 40 grams collected, m. p. 62°–63°. It gave percentages of carbon and hydrogen indicating the series $C\ H_{2n+2}$.

0.1520 gram solid gave 0.4752 gram CO_2 and 0.2062 gram H_2O.

	Calculated for $C_{29}H_{60}$.	Found.
C	85.28	85.27
H	14.72	14.87

Molecular weight determinations:

I. 1.6181 gram substance and 23.57 grams benzene gave a rise of 0°.41.

II. 1.6236 grams substance and 23.99 grams benzene gave a rise of 0°.402.

Calculated for $C_{29}H_{60}$.	Found. I.	Found. II.
406	405	408

The solid distilling above 350° has the composition of the series C_nH_{2n+2} as shown by analysis:

0.1469 gram solid gave 0.4581 gram CO_2 and 0.1947 gram H_2O.

	Calculated for $C_{30}H_{62}$.	Found.
C	84.31	85.04
H	14.69	14.82

Because only 2 per cent of the original paraffin taken for distillation remained as a residue at 350°, the solid hydrocarbons composing the main body of paraffin produced in the refinery are evidently members of the series C_nH_{2n+2}. They do not contain oxygen, as is frequently stated, at least not those that can be distilled. It is not reasonable to assume that they have been formed from other constituents by "cracking," because such decompositions give rise to hydrocarbons of lower molecular weight. It is well known that paraffin, when exposed to air, may be decomposed completely by heat into lower hydrocarbons. In mass we have found that it may be distilled indefinitely by exclusion of air, but it cannot be distilled in air without decomposition.

Thorpe and Young[1] subjected shale paraffin to distillation, under pressure, in a bent tube so arranged that the paraffin could be repeatedly distilled. The distillation was continued until the solid was converted into bodies that remained liquid at ordinary temperatures. This liquid proved to consist of two series of hydrocarbons; of the series C_nH_{2n+2}, the hydrocarbons C_6H_{14} to $C_{11}H_{24}$ were identified and of the series C_nH_{2n} the ethylene hydrocarbon compounds C_5H_{10} to $C_{11}H_{22}$.

It is our intention to examine the products of the distillation of paraffin in air to observe the changes in "cracking". It is an interesting question as to whether any relation exists between the paraffin hydrocarbons and the methylenes, with reference to the organic origin of these bodies and whether the series are interconvertible by natural agencies.

[1] Ber. d. chem. Ges., **5**, 556 (1872).

Hydrocarbons in Commercial Paraffin.

	Formula.	Melting-points.	Specific gravity.
Tricosane	$C_{23}H_{48}$	48°	0.7886 at 60°
Tetracosane	$C_{24}H_{50}$	50°–51°	
Pentacosane	$C_{25}H_{52}$	53°–54°	0.7941 at 60°
Hexacosane	$C_{26}H_{54}$	55°–56°	0.7968 at 60°
Octocosane	$C_{28}H_{58}$	60°	
Nonocosane	$C_{29}H_{60}$	62°–63°	

VII. COMPOSITION OF COMMERCIAL VASELINE, COSMOLINE, AND SIMILAR PRODUCTS.

After ascertaining the composition of the constituents of Pennsylvania petroleum with high boiling-points and the composition of the semi-solid product used at Coreopolis for the manufacture of the medicinal preparations, it seemed of interest to investigate the composition of the commercial products for comparison with specimens obtained directly from the wells. On account of the very high boiling-points, it is only possible to distil *in vacuo*. Under 15 mm., 100 grams of vaseline (Ceroleum) distilled in the following proportions:

	–250°.	250°-275°.	275°-300°.	300°-325°.	325°-350°.	350°-360°.	Residue.
Grams	14	22	14	18	7	20	6

The distillates were light-yellow and, when melted, showed a slight fluorescence. Below 250° the distillate was a heavy, viscous liquid, the others all semi-solid and the residue was brown. To ascertain whether solids could be separated from these distillates, the fraction 250°–275° was dissolved in ether and sufficient alcohol added to precipitate the solid hydrocarbon. The solid was again dissolved in ether and precipitated by alcohol. After filtration it had no greasy feel and melted at 70°. From the fraction 350°–360°, after similar treatment, a solid was obtained which melted at 77°–78°. These substances resembled in all respects the solid paraffin hydrocarbons. It is, therefore, evident that vaseline is composed of heavy oils such as have been identified as forming the portions of Pennsylvania petroleum with high boiling-points, and Coreopolis heavy oil, hydrocarbons of the series C_nH_{2n}, C_nH_{2n-2} and C_nH_{2n-4}, together with solid paraffin hydrocar-

bons. The quantity of solid paraffins is sufficient to saturate the oil and, in slight excess, to form an emulsion of the desired consistency.

What is known as "scale" paraffin in the refineries is composed of solid hydrocarbons, with enough of the heavy oils to form a greasy solid. But the solid constituents are hydrocarbons of the same series, C_nH_{2n+2}, which cannot be changed into other forms without decomposition. These hydrocarbons are only sparingly soluble in the liquid hydrocarbons of lower boiling-points of the same series, but they dissolve more freely in the series with high boiling-points, C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2} and C_nH_{2n-4}.

Since the work described in these papers was begun ten years ago, I have received efficient aid from the following assistants: in distillation, Messrs. C. Lindmueller, D. H. Walker, C. R. Cummins, and H. A. Triebing; in distillation and analysis, Mr. C. S. Richards; analysis and molecular weight determinations, Mr. O. J. Sieplein.

It is my intention to make later a summarization, in a separate communication, of the results published from the beginning in this series of papers on petroleum.

Contributions from the Chemical Laboratory of Harvard College.

ON 4-NITRO-5-PYRAZOLONE.[1]

By H. B. Hill and O. F. Black.

During an investigation of the oximes of nitromalonic aldehyde, W. J. Hale and one of us[2] made the observation that, when nitromalonic diacetyldialdoxime,

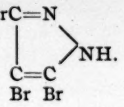
$$CH_3COONCHCHNO_2.CHNOCOCH_3,$$

was dissolved in a hot solution of sodic hydrate, the sodium salt of a new acid was formed, which was shown, by the analysis of its silver salt, to be an isomer of fulminuric acid, $C_3H_3N_3O_5$. The results of the further study of this substance are contained in the following paper.

[1] Most of the work described in this paper was done under the direction of Professor Hill, but it was finished and the paper written after his lamented death. C. L. J.

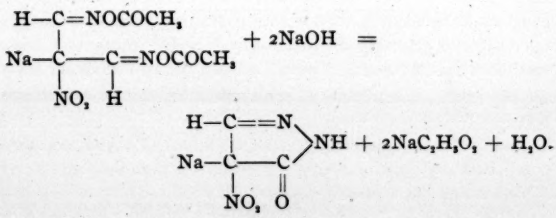
[2] This Journal, **29**, 253 (1903).

The substance, $C_3H_3N_3O_3$, melted at 136°–137° and formed well-defined salts, of which the sodium salt, $NaC_3H_2N_3O_3.3H_2O$, the silver salt, $AgC_3H_2N_3O_3$, the barium salt, $Ba(C_3H_2N_3O_3)_2.4H_2O$ and the lead salt, $Pb(C_3H_2N_3O_3)_2$, were analyzed. By the action of a stream of air, loaded with bromine vapor, on the aqueous solution of the sodium salt a new compound, $C_3HN_2Br_3$, was obtained, which was remarkably stable, as it sublimed unaltered and was not decomposed by long boiling with sodic hydrate in strong aqueous solution nor even with an alcoholic solution. These properties indicated a ring-shaped structure for the molecule and in that case the formula would show that the substance is tribrompyrazol,



Its observed properties agree with this theory of its constitution, as it dissolves even in weak solutions of the alkalies and is precipitated unaltered by acids; it forms an unusually stable silver salt and with sodium amalgam it gives a purple color.

The bromine derivative being established as a substituted pyrazol, it was probable that the sodium salt, $NaC_3H_2N_3O_3$, from which it was made, also had a ring structure and would probably be the 4-nitro-5-pyrazolone, which could be formed from the nitromalonic diacetyldialdoxime by the following reaction:



To test this theory we tried the action of phosphoric oxy-

chloride on our sodium salt, since Michaelis and Röhmer[1] have shown that this reagent converts many pyrazolones into the corresponding chlorpyrazol; upon heating the substances together, in a sealed tube, at 100°, we obtained 4-nitro-5-chlorpyrazol, agreeing, in melting-point and properties, with that made by Oskar Meder[2] by the action of nitric acid on 5-chlorpyrazol. Meder gives the melting-point 185°–188°; we found 186°–187°. There can be no doubt, therefore, that our salt is the sodic 4-nitro-5-pyrazolone and this theory is confirmed by its properties, especially by the fact that it turns purple when treated with sodium amalgam.

A secondary product of the preparation of the tribrompyrazol was obtained in too small quantity for thorough study. A single determination of bromine indicated that it might be a dibromnitropyrazol.

EXPERIMENTAL PART.

Preparation of Sodic Nitromalonic Diacetyldialdoxime.—This substance[3] was prepared as follows: Six grams of the hydrochlorate of hydroxylamine, dissolved in 20 cc. of 5N sodic hydrate, were mixed with 6 grams of the sodium salt of nitromalonic aldehyde, dissolved in 20 cc. of water and the mixture allowed to stand until crystals of the sodic dialdoxime began to appear. Twenty cc. of 5N sodic hydrate were then added, the liquid diluted with about one-half its volume of water and poured into eight test-tubes, which were kept cooled by immersion in ice-water. Small quantities of acetic anhydride were added to each test-tube in turn and the contents shaken until the mixture became nearly solid from the formation of the light-yellow, finely-crystalline precipitate of the diacetyl body, which was then washed with cold water, filtered on the pump and dried on a porous plate. The yield of sodic nitromalonic diacetyldialdoxime averaged 9 grams.

Sodic 4-Nitro-5-pyrazolone, $NaC_3H_2N_3O_3$.—To prepare this compound 2.53 grams of the dry sodic nitromalonic diacetyl-

[1] Ber. d. chem. Ges., **31**, 2908 (1898).

[2] Inaug. Diss., Jena, 1901. We cannot find that this work has been published in any journal.

[3] Hill and Hale: THIS JOURNAL, **29**, 264 (1903).

dialdoxime were added to 20 cc. of sodic hydrate, previously warmed in a porcelain dish on the water-bath; these weights give 2 molecules of sodic hydrate for each molecule of the diacetyl body. The bright red solution thus obtained, after evaporation to about one-half its volume on the steam-bath, yielded, on cooling, a mass of fine orange-yellow needles of the new salt. This, however, could not be purified conveniently for analysis by recrystallization from water, as it was very hard to remove, in this way, a small impurity of sodic acetate, which has about the same solubility in water as the new substance. The specimens for analysis were therefore prepared by neutralizing, with pure sodic hydrate, the pure acid made in the manner described later in this paper:

0.3276 gram salt, dried on filter-paper, lost 0.0573 gram when exposed to the air.

	Calculated for $NaC_3H_2N_3O_3.3H_2O$.	Found.
$2H_2O$	17.56	17.50

0.1972 gram air-dried salt lost 0.0203 gram at 120°.

	Calculated for $NaC_3H_2N_3O_3.H_2O$.	Found.
H_2O	10.65	10.30

From these analyses it appears that the salt contains 3 molecules of water, two of which are given off on exposure to the air. The third molecule was removed by heat, but not by drying over sulphuric acid.

I. 0.1998 gram salt, dried *in vacuo* over sulphuric acid, gave 0.0844 gram Na_2SO_4.

II. 0.1769 gram salt, dried at 120°, gave 0.0834 gram Na_2SO_4.

	Calculated for		Found.	
	$NaC_3H_2N_3O_3.H_2O$.	$NaC_3H_2N_3O_3$.	I.	II.
Na	13.61	15.23	13.69	15.29

It crystallizes, by spontaneous evaporation from water, in dark-red prisms, which effloresce in the air, losing finally 2 molecules of water. It is soluble in water and sparingly soluble in alcohol. When treated with sodium amalgam, the reduced product turns purple on exposure to air.

4-Nitro-5-pyrazolone.—This substance was made by adding hydrochloric acid to a solution of the sodium salt in water and extracting with ether. On the addition of ligroin to the ethereal solution the body was deposited in small, colorless crystals, which melt at 136°–137°. It is soluble in water, alcohol, or ether, less soluble in benzol, chloroform, or ligroin. It was not analyzed, but, as the specimens of the sodium salt which were analyzed were made from it, there can be no doubt about its composition.

Argentic 4-Nitro-5-pyrazolone, $AgC_3H_2N_3O_3$.—This salt was made by adding argentic nitrate either to the sodium salt or to the free pyrazolone. The precipitate from the sodium salt was washed with water and dried *in vacuo* for analysis.

I. 0.2229 gram substance gave 0.1774 gram AgBr.

II. 0.2358 gram substance gave 37.6 cc. N_2 at 22°.3 and 759.5 mm.

	Calculated for $AgC_3H_2N_3O_3$.	Found. I.	II.
Ag	45.74	45.71	. .
N	17.79	. .	17.84

The salt forms a reddish-yellow powder, insoluble in cold or hot water.

Baric 4-Nitro-5-pyrazolone, $Ba(C_3H_2N_3O_3)_24H_2O$.—This was made direct from the sodic nitromalonic diacetyldialdoxime by heating on the steam-bath an aqueous solution of that substance and baric hydrate, in the proportion of one molecule of each. The barium salt crystallized from the dark-red solution and was purified by recrystallization from hot water and dried on filter-paper for analysis.

1.0767 grams salt lost 0.1682 gram at 120°.

	Calculated for $BaC_6H_4N_6O_{14}H_2O$.	Found.
H_2O	15.47	15.63

0.2365 gram salt, dried at 120°, gave 0.1402 gram $BaSO_4$.

	Calculated for $BaC_6H_4N_6O_{14}$.	Found.
Ba	34.93	34.89

It crystallizes in dark-red, efflorescent needles and is somewhat less soluble in water than the sodium salt, but otherwise resembles it closely.

Plumbic 4-Nitro-5-pyrazolone, $Pb(C_3H_2N_3O_3)_2$.—This salt was obtained, as a yellow precipitate, by adding a solution of plumbic acetate to one of the sodium salt. It was washed with cold water and dried *in vacuo* for analysis.

0.2655 gram salt gave 0.1741 gram $PbSO_4$.

	Calculated for $PbC_6H_4N_6O_8$.	Found.
Pb	44.71	44.78

It forms a yellow powder only slightly soluble in hot water and nearly insoluble in the cold.

An acetylpyrazolone was made by shaking a solution of the sodium salt and sodic hydrate with acetic anhydride when the new compound was deposited as a white crystalline precipitate. After crystallization from a mixture of chloroform and ligroin it formed small, colorless prisms melting at 129°. Boiling with sodic hydrate converts it into the sodium salt again. It was not analyzed.

4-Nitro-5-chlorpyrazol, $C_3H_2N_3ClO_2$. — This substance was prepared from the 4-nitro-5-pyrazolone by heating it to 100°, in a sealed tube, with excess of phosphoric oxychloride. As the tube cooled the pyrazol crystallized out in needles, which were washed with cold water, recrystallized once from hot water and dried *in vacuo* for analysis.

0.2017 gram substance gave, by the Carius method, 0.2002 gram AgCl.

	Calculated for $C_3H_2N_3ClO_2$.	Found.
Cl	24.07	24.57

It forms fine white[1] needles, which melt at 186°–187°. It is freely soluble in alcohol or acetone; slightly soluble in ether chloroform; slightly soluble in cold or freely soluble in hot water. These properties agree with those given by Oskar Meder (Inaug. Diss., Jena, 1901) for this substance, which he

[1] The compound, prepared as described, had a yellowish color, which was removed by treatment with bone-black.

prepared in a different way. His melting-point was 185°–188°.

Tribrompyrazol, $C_3HN_2Br_3$.—When a stream of air, loaded with the vapor of bromine, was passed through a solution of the sodic 4-nitro-5-pyrazolone, a white flocculent precipitate was gradually formed, which consisted principally of tribrompyrazol, but, as it also contained a yellow gummy impurity, it is better to prepare the tribrompyrazol as follows: The sodic 4-nitro-5-pyrazolone, dissolved in a few cubic centimeters of strong hydrobromic acid, was mixed with an excess of bromine and heated in a sealed tube, to 100°, for two or three hours; in this way a good yield of fine, white needles was obtained. It was purified by washing with cold water and distillation with steam, dried *in vacuo* and analyzed:

I. 0.2158 gram substance gave 0.0920 gram CO_2 and 0.0140 gram H_2O.

II. 0.2863 gram substance gave 0.1240 gram CO_2 and 0.0140 gram H_2O.

III. 0.2351 gram substance gave 19.1 cc. N_2 at 24° and 762 mm.

IV. 0.1614 gram substance gave, by the Carius method, 0.2985 gram AgBr.

	Calculated for $C_3HN_2Br_3$.	Found. I.	II.	III.	IV.
C	11.79	11.63	11.81	. .	. .
H	0.31	0.74	0.54	. .	. .
N	9.18	. .	. .	9.13	. .
Br	78.65	. .	. .	. .	78.69

Properties of Tribrompyrazol.—It forms silky, white needles, which collect in matted masses looking like cotton. It melts at 181°, but sublimes at 120° or perhaps at a somewhat higher temperature. It distils with steam and is soluble in alcohol or ether; sparingly soluble in hot water, essentially insoluble in cold. It dissolves in sodic hydrate solution and is precipitated on the addition of an acid. When treated with sodium amalgam, the reduced product takes on a characteristic purple color on exposure to the air.

Argentic Tribrompyrazol, $AgC_3N_2Br_3$.—This salt was made by adding argentic nitrate, dissolved in water, to a solution of

tribrompyrazol in dilute alcohol, when a finely crystalline precipitate was formed which was washed with water and dried at 100° for analysis. The yield was quantitative. All our attempts to analyze it by the method of Carius failed, because we found it impossible to decompose it completely with nitric acid; we accordingly resorted to the electrolysis of the salt dissolved in potassic cyanide.

0.3246 gram salt gave 0.0843 gram Ag.

	Calculated for $AgC_3N_2Br_3$.	Found.
Ag	26.21	25.97

The salt forms a white crystalline powder, insoluble in hot water. It is slightly soluble in hot, strong nitric acid, but separates from the solution almost completely on cooling. It is a very stable substance, as it is not decomposed completely even when heated to 300°, with fuming nitric acid.

The acetyltribrompyrazol was made by dissolving tribrompyrazol in a solution of sodic hydrate and shaking the cooled mixture with acetic anhydride. It crystallizes from hot alcohol in white, felted needles, melting at 105°–106°. Boiling with water converts it again into tribrompyrazol. It was not analyzed.

Secondary Product Formed in Making Tribrompyrazol.—When the tribrompyrazol was prepared by the action of bromine vapor on sodic 4-nitro-5-pyrazolone, another substance was formed in small amount. This was obtained by concentrating the mother-liquors from the tribrompyrazol to a small volume. On cooling, the new compound separated in white crystals, which, however, were very impure. It was found that the best way to purify it consisted in further treatment with bromine, which formed an orange crystalline addition-compound; by boiling this with water, bromine was given off and the original white body was left in a state of purity. It was dried *in vacuo* for analysis.

0.1632 gram substance gave, by the Carius method, 0.2277 gram AgBr.

	Calculated for $C_3HBr_2N_3O_2$.	Found.
Br	59.03	59.35

The result of this analysis agrees very well with the percentage of bromine in a dibromnitropyrazol, but it is obvious that more analytical work is needed before this formula can be considered established. It crystallizes in white needles, melts at 163°–164° and forms an acet compound, when treated with acetic anhydride and sodic hydrate.

Some of the bromine addition-product, made by the action of bromine on the substance just described, was washed with cold water, dried rapidly by pressing on filter-paper and analyzed.

0.1778 gram substance gave, by the Carius method, 0.2839 gram AgBr.

	Found.
Br	67.93

This result agrees excellently with that calculated for the addition of 1 molecule of bromine to 2 molecules of the dibromnitropyrazol; $C_6H_2Br_4N_4O_4$ contains 68.37 per cent of bromine. The analysis, however, is not entitled to much consideration, unless confirmed by additional work, as the substance loses bromine when exposed to the air and also by boiling with water, so that, even during the washing with cold water, some bromine might have been lost and there was certainly danger of such a loss during the drying and weighing. The addition-compound forms hard, orange crystals, insoluble in cold water, but decomposed by boiling with water with evolution of bromine and the formation of the white substance melting at 163°-164°. We regret that we were unable to complete the investigation of these substances.

CAMBRIDGE, November 26, 1904.

Contributions from the Chemical Laboratory of Harvard College.

PURE NITROGEN FROM NITROUS AND NITRIC OXIDES AND AMMONIA.

BY GREGORY PAUL BAXTER AND CHARLES HENDER HICKEY.

The preparation of nitrogen from ammonium nitrite necessitates subsequent purification from oxygen and oxygen compounds, by passing it over hot copper and offers many prac-

tical difficulties in the production of a regular and continuous current of gas. Nitrogen made from the air, by removing the oxygen with hot copper, with or without the addition of ammonia, contains about 1 per cent of argon, besides, of course, traces of the other inert gases. Hence a method of preparing nitrogen, at will, in large quantities, free from other gases, is likely to be of practical use. Such a method is described below.

Both nitrous and nitric oxides, when mixed with ammonia and ignited, combine with the latter gas to form nitrogen and water. In the case of nitrous oxide this combination takes place with almost the violence of an oxyhydrogen explosion.[1] In the case of nitric oxide, on the other hand, combination is complete only when the mixture is heated to a high temperature in the presence of a catalytic agent. Although, according to the equations

$$3N_2O + 2NH_3 = 4N_2 + 3H_2O,$$
$$6NO + 4NH_3 = 5N_2 + 6H_2O,$$

the volume of nitrogen which may be obtained from a given volume of nitrous oxide is almost double that which can be obtained from the same volume of nitric oxide, the ease with which nitric oxide may be prepared more than counterbalances the comparatively small yield of nitrogen. Hence the reaction with nitric oxide was investigated first.

The apparatus used in the experiments was as follows: A regular stream of nitric oxide was generated by dropping nitric acid, specific gravity about 1.2, upon copper turnings. This gas was conducted through a gas washing-bottle, containing strong ammonia, into a hard glass tube which contained two four-inch rolls of copper gauze, to act as the catalyzer. The tube was heated by a combustion furnace. The copper rolls remained perfectly bright during the experiment, indicating that ammonia was in excess and the gas which resulted, when collected over water, so that the excess of ammonia was ab-

[1] Dammer states that mixtures of ammonia and nitrous oxide explode when either ignited or sparked and that mixtures of ammonia and nitric oxide explode only when sparked, while at lower temperatures nitrogen, nitrogen oxides and water are produced. Handb. d. anorg. Chem., II., 1, 34, 38.

sorbed, gave no evidence of nitric oxide by its odor. In order, however, to make certain of the purity of the nitrogen, the gas was subjected to the following test: It was first conducted through a solution of dilute sulphuric acid to remove the greater part of the ammonia; then through one Emmerling tower, containing fused stick potassium hydroxide, and two towers with glass pearls moistened with concentrated (freshly boiled) sulphuric acid, to remove moisture and the last traces of ammonia; after the gas had removed every trace of air, a small hard-glass tube, containing a roll of bright copper gauze, was connected with the last sulphuric acid column. The air in this tube was swept out and the copper heated with a full Bunsen flame. As no visible change in the appearance of the copper gauze had taken place at the end of one hour, it was evident that no nitric oxide remained in the nitrogen.

The well-known catalytic power of finely divided platinum led to a repetition of the above experiment, with platinized asbestos instead of copper. In one case, where poorly platinized asbestos was employed, some nitric oxide remained unattacked. A second attempt, with 2 inches of thoroughly platinized asbestos, resulted as successfully as in the case of copper.

Experiments were then carried out to determine the minimum concentration of ammonia solution in which the tension of ammonia was sufficiently large to yield, to the nitric oxide, an excess of ammonia over that necessary for the reaction. It was found that the nitric oxide was not completely acted upon if the specific gravity of the ammonia was above 0.925. Of course the minimum concentration of ammonia varies somewhat with temperature, with the rate at which the nitric oxide passes through the solution and with the form of the bottle containing it.

The use of copper, in the preparation of nitric oxide, makes the method somewhat expensive. Iron turnings mixed with a few small pieces of platinum were found to serve equally well. Small quantities of nitrous oxide or nitric peroxide, as impurity in the nitric oxide, could do no harm.

The following precautions are the most important in the successful production of pure nitrogen by this method.

1. The temperature of the catalytic agent must not be too low. Experiments where kerosene stoves were employed with the copper rolls showed only partial combination of the gases.

2. The ammonia should not be allowed to fall below the concentration corresponding to the sp. gr. 0.92.

3. If absolutely pure nitrogen is desired the materials must be purified. The metal used for the production of nitric oxide must be free from grease, the ammonia must be separated from amines and the purifying solutions must be boiled to expel air. The apparatus must be constructed entirely of glass, to avoid the introduction of sulphur and organic matter from the rubber.

Finally, a method was sought by which the explosion of the mixture of nitrous oxide and ammonia could be avoided. Nitrous oxide, when heated to a high temperature, decomposes into nitrogen and oxygen,[1] which do not explode when ignited with ammonia. The following apparatus was used for effecting this decomposition and for removing the oxygen by means of ammonia:

Nitrous oxide, produced by heating ammonic nitrate, was conducted through a short, hard glass tube in which a 2-inch section of platinized asbestos was heated to dull redness. The gases then passed through a wash-bottle containing concentrated ammonia solution. As the mixture showed no tendency to explode when ignited, it was considered safe to effect the reaction by conducting it through a second hard-glass tube, also containing a section of heated platinized asbestos. Complete combustion of the oxygen took place, for, when the resulting gas was freed from ammonia and water, as described above, a bright copper roll heated in it for some time remained unchanged.

The precautions to be observed in the use of the nitrous oxide are essentially the same as those mentioned in the case of nitric oxide. The platinized asbestos should be heated to as high a temperature as the hard-glass tubes will allow. "Blowing out" of the tubes may be prevented by wrapping the heated section in asbestos paper, to distribute the heat. The ammonia must not be too dilute, but more dilute ammo-

[1] Dammer: Handb. d. anorg. Chem., II., 1, 34.

nia may be employed here than in the case of nitric oxide, on account of the increase in volume when nitrous oxide is decomposed into nitrogen and oxygen.

CAMBRIDGE, MASS.,
Dec. 2, 1904.

REPORT.

The Grignard Reaction.

Since the discovery of the compounds of zinc with organic radicals by Frankland[1], these substances have been of great assistance in organic synthesis, the similar sodium and mercury derivatives being of secondary importance. This is not the place to give an account of the difficulties met with in preparing and using these compounds, but so many investigators have entered the field opened by Grignard, that it is evident there was room for improvement in the old method.

Barbier[2] allowed methylheptenone,

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-CO-CH_3,$$

to act on methyl iodide, in the presence of magnesium and obtained the tertiary alcohol, dimethyl-2,6-heptene-2-ol-6. This was surprising, for the zinc alkyls do not yield tertiary alcohols when they react with ketones and the method of Saytzeff, which was employed, is not applicable to ketones with the grouping $-CO-CH_3$.

Grignard[3] undertook a general study of this and similar reactions. He soon found that magnesium is much more reactive than zinc and can be employed in many cases where the latter metal is useless. At first an attempt was made to isolate the organo-magnesium compounds, but this was soon abandoned. The work of Löhr,[4] Fleck[5] and of Waga[6] showed that they are solids which are extremely unstable and act on alcohol and water with violence. They take fire in the air, or even in dry carbon dioxide and the only neutral solvent that can be used is a mixture of benzene and ether. The solution does not lend itself readily to reactions, besides which, the com-

[1] Ann. Chem. (Liebig), **85**, 329 (1853). Phil. Trans., **142**, 417 (1852).
[2] Compt. rend., **133**, 110.
[3] Ann. Chim. Phys., [7], **24**, 433 (1901).
[4] Ann. Chem. (Liebig), **261**, 72.
[5] *Ibid.*, **276**, 129.
[6] *Ibid.*, **282**, 320.

pounds could not be made conveniently, except by heating the alkyl iodides, in sealed tubes, with magnesium amalgam.

Frankland[1] and Wanklyn[2] had obtained substances such as $Zn(C_2H_5)_2.O(C_2H_5)_2$, etc., by heating zinc, an alkyl iodide and anhydrous ether, in sealed tubes. These compounds acted like the corresponding zinc alkyls. The reaction was, however, very incomplete and the reaction-product had to be distilled, as in the ordinary procedure, to effect a separation from the large solid mass that was formed.

With magnesium, which is much more strongly electropositive than zinc, we should expect the reaction to be more nearly complete and this was found to be the case. At the ordinary temperature, magnesium attacks methyl iodide, the reaction is complete and the product is soluble in ether. The method of work is comparatively simple. A mixture of the organic halide and anhydrous ether is allowed to drop slowly upon the calculated amount (1 molecule) of magnesium turnings, contained in a flask, provided with a return-condenser. Action begins at once and it is necessary to moderate it by cooling the flask. When all the magnesium has been dissolved, it is found that almost exactly 1 molecule of the halide has been used for each molecule of the metal. After warming a short time on the water-bath, the reaction-product is a nearly colorless liquid, containing a little dark powder, originating from traces of iron. Grignard found that the reaction took place with methyl, isopropyl, tertiary butyl and secondary hexyl iodides, with ethyl, propyl, isobutyl, isoamyl and benzyl bromides, as well as with brombenzene and bromnaphthalene. The ethereal solution thus obtained reacts violently with water, forming magnesium hydroxide and it is changed by moist air. Carbon dioxide acts upon it, giving a crystalline deposit. It acts energetically upon aldehydes, ketones and with the chlorides and anhydrides of acids. As the vapor of ether fills the apparatus, it is not necessary to work in an atmosphere of an inert gas. This is a great advantage over the zinc compounds.

There are two possible reactions between the organic halide and magnesium:

$$(1)\quad CH_3I + Mg = CH_3MgI,$$

and

$$(2)\quad 2CH_3I + 2Mg = (CH_3)_2Mg.MgI_2.$$

If the reaction is according to (2) the product cannot be $(CH_3)_2Mg + MgI_2$, for it has been shown that magnesium methyl is practically insoluble in ether[3] and magnesium iodide

[1] Phil. Trans., 140, 412 (1859).
[2] J. Chem. Soc. (London), 13, 125 (1861).
[3] Löhr: Ann. Chem. (Liebig), 261, 72. Fleck: *Ibid.*, 276, 129.

is also. Whether (1) or (2) is correct, we should obtain, in each case, 1 molecule of a saturated hydrocarbon for each molecule of halide, when water is allowed to act upon the product, thus:

(1) $2CH_3MgI + 2H_2O = 2CH_4 + MgI_2 + Mg(OH)_2$,

or

(2) $(CH_3)_2Mg.MgI_2 + 2H_2O = 2CH_4 + MgI_2 + Mg(OH)_2$.

Experiment showed that methane was obtained in almost the theoretical amount.

When the ether was driven off by heating on the water-bath, an extremely viscous, dark gray mass remained. It contained some ether and its appearance was not changed even after heating for two days at 50° (10–12 mm.). It was then heated at 80° for three days, with frequent shaking, to renew the surface. Under these conditions the thinner parts, on the walls of the flask, became dry and had a light-brown tint, but the main portion consisted of a gum that could not be removed without breaking the flask. The dried substance changed rapidly in the air, becoming warm and reacted very violently with water. The methyl iodide compound was found to have the composition $CH_3MgI + \frac{2}{3}(C_2H_5)_2O$, and the ethyl bromide derivative was $C_2H_5MgBr + 28$ grams $(C_2H_5)_2O$. To remove the last traces of ether it was necessary to heat at 150°, in a vacuum, for several days. In this state the compounds were insoluble in anhydrous ether and seemed to be identical with those described by Löhr.[1]

The tenacity with which they retain ether seems to show that it is held in much the same way as water of crystallization. Frankland[2] obtained the analogous derivatives,

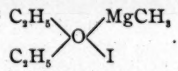
$$Zn(CH_3)_2.(C_2H_5)_2O \quad \text{and} \quad Zn(CH_3)_2.(CH_3)_2O.$$

The formation of these compounds is not unimportant, for, in the presence of benzene, ligroin, or other neutral solvent, the halogen compounds do not attack magnesium. On the other hand, the reaction goes very well in the presence of the different oxygen ethers, such as anisol and methyl isoamyl ether. Besides, the molecule of ether of crystallization makes the compounds soluble. It does not, however, enter into the reaction when the compounds are treated with ketones, etc.

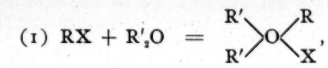
According to Schmidt[3] these substances are derivatives of

[1] *Loc. cit.*
[2] Phil. Trans., 149, 412 (1859).
[3] "Die basische Eigenschaften des Sauerstoffs und Kohlenstoffs," p. 17.

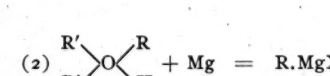
tetravalent oxygen, or, in other words, they are oxonium compounds. For example :

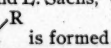


In a recent paper[1], Tschelinzeff gives his reasons for thinking that the ether simply plays the part of a catalytic agent. He found that the reaction takes place in the presence of very small quantities of ether, or anisol and, in some cases, even that may be dispensed with when bromides or iodides are used. Further, by working at a comparatively high temperature, a few halides yield the corresponding organo-magnesium compounds when neither ether nor benzene is present. Hence the reaction is typically catalytic, the ether simply favoring the dissociation of the halide and thus enabling the reaction to proceed more easily and at a lower temperature. He expresses it thus :

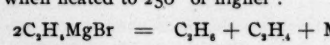


and



In an earlier paper[2] he showed that dimethylaniline or some other tertiary amine could be used in place of the ether and in this was confirmed by F. and L. Sachs,[3] who used quinoline. Tschelinzeff found that  is formed, analogous to and the reaction goes so smoothly that he recommends the use of dimethylaniline, or other tertiary amine, in place of ether. The mixture is warmed until the reaction begins, or the liquid boils. At times a small crystal of iodine is used to start the action.

Grignard found that the compounds decompose with violence when heated to 250° or higher :



[1] Ber. d. chem. Ges., **37**, 4534 (1904).
[2] *Ibid.*, **37**, 2081 (1904).
[3] *Ibid.*, **37**, 3089 (1904).

The reaction does not proceed as smoothly as the equation indicates; the magnesium set free is at once oxidized by the traces of air in the flask.

Because the organo-magnesium halides are soluble in ether, react with water and acids without incandescence and do not take fire in the air, it is certain that they do not contain the grouping $Mg(CH_3)_2$ or $Mg(C_2H_5)_2$. If, to the product from one molecule each of magnesium and halide, we add one molecule of an aldehyde, there is obtained 0.6–0.8 molecule of a secondary alcohol. The reactions may take place as follows:

I.

$$(CH_3)_2Mg + RCHO = RC(OMgCH_3)(H)(CH_3),$$

and

$$RC(OMgCH_3)(H)(CH_3) + 2H_2O = RC(OH)(H)(CH_3) + Mg(OH)_2 + CH_4,$$

or

II.

$$CH_3MgI + RCHO = RC(OMgI)(H)(CH_3),$$

and

$$2RC(OMgI)(H)(CH_3) + 2H_2O = 2RC(OH)(H)(CH_3) + MgI_2 + Mg(OH)_2.$$

According to (I) there should be an evolution of gas when water is added. "In the second case the compound that is formed contains all the halogen that was introduced; in the first case, on the contrary, it does not contain a trace, for it

seems very probable that, if the grouping MgI_2 existed in the organo-magnesium compound it would be precipitated on combining with the aldehyde or ketone" (Grignard). Further, each molecule of halide should yield 0.5 molecule of alcohol, according to (I). As a matter of fact, no gas is ever evolved on adding water, the compounds are soluble in ether, or homogeneously crystalline (apparently without separation of magnesium iodide) and the yield is from 0.6–0.8 molecule of alcohol. Hence it seems most probable that the actual course of the reaction is as represented by (II.).

A secondary reaction takes place when magnesium is acted upon by the halogen derivative of a hydrocarbon. To a certain extent the metal acts like sodium in Wurtz's reaction, causing the formation of higher hydrocarbons, the amount of which depends on the number of carbon atoms in the halide. With isobutyl bromide the quantity of diisobutyl is usually too small to be purified; with isoamyl bromide the yield of diisoamyl is 10–15 per cent; with benzyl bromide the amount of hydrocarbon is 30–35 per cent, while with hexyl iodide there is formed about 50 per cent of dihexyl. Comparing the two reactions,

$$\text{I.}\quad RBr + Mg = RMgBr,$$

and

$$\text{II.}\quad 2RBr + Mg = MgBr_2 + R{-}R,$$

we see that, according to I, each molecule of halide requires one atom of magnesium, while if the reaction takes place as shown by II, only 0.5 atom of magnesium is needed for each molecule of halide. Grignard tried to suppress the secondary reaction as much as possible by using finer magnesium turnings, but no great difference was noticed in the results. It is useless to try to increase the exposed surface of metal by using magnesium powder, for it is always too much oxidized. Secondary halides showed a greater tendency to yield higher hydrocarbons than the corresponding primary ones and this was still more pronounced in the case of the tertiary halides. Tertiary butyl iodide gave a large amount of hydrocarbon, while nearly half of the magnesium was unchanged. Other methods for the preparation of hydrocarbons will be given later.

Löhr,[1] Fleck[2] and Waga[3] stated that the symmetrical organo-magnesium compounds take fire in carbon dioxide. Grignard found that the gas also acts on the symmetrical compounds, but not violently, so that the reaction could be studied. If a current of the gas is passed into an ethereal solution of magne-

[1] Ann. Chem. (Liebig), **261**, 72.
[2] *Ibid.*, **276**, 129.
[3] *Ibid.*, **283**, 330.

sium methyl iodide, a crystalline deposit is at once formed. The reaction-mixture is poured upon crushed ice, acidified with dilute sulphuric acid and extracted with ether. The product is acetic acid. Isovaleric acid was made from isobutyl bromide. The following equations express the changes :

$$RMgBr + CO_2 = R{-}C(=O){-}OMgBr,$$

and

$$2R{-}C(=O){-}OMgBr + xH_2O = (RCO_2)_2Mg + MgBr_2 + xH_2O.$$

Similar reactions take place with organo-sodium compounds, but they are of greater theoretical interest than practical importance.[1]

Numerous other chemists have used this reaction since it was first applied by Grignard. Zelinsky[2] found that hydroaromatic and cyclic hydrocarbons yield acids according to the reactions given above. He recommends, as an interesting lecture experiment,[3] the preparation of benzoic acid from phenyl iodide. Schroeter[4] found that, when phenyl bromide is used, the chief products are triphenylcarbinol, benzophenone, a little benzoic acid and a new compound which he did not identify. Houben and Kesselkaul[5] and Bodroux also prepared acids by means of the reaction. The last author started with dihalogen derivatives of the aromatic hydrocarbons and found that only one of the halogen atoms reacts.[6] From the monobromine derivatives of anisol and β-methoxynaphthalene he obtained the acids in which bromine is replaced by carboxyl.[7] Houben and Kesselkaul found that carbon disulphide can be used in place of carbon dioxide.[8] Among other acids they prepared phenyldithioacetic acid, $C_6H_5CH_2CS_2H$.

With carbonyl chloride[9] tertiary alcohols are obtained, according to the equations :

[1] Wanklyn : Ann. Chem. (Liebig), **107**, 125 ; **111**, 234. Kekulé : *Ibid.*, **137**, 180. R. Meyer u. Muller : Ber. d. chem. Ges., **15**, 496, 698, 1905. Wanklyn and Schenk : Ann. Chem. (Liebig), Suppl., **6**, 120.
[2] Ber. d. chem. Ges., **35**, 2687.
[3] *Ibid.*, **35**, 2692.
[4] *Ibid.*, **36**, 3005.
[5] *Ibid.*, **35**, 2519.
[6] Bull. Soc. Chim., [3], **31**, 24 (1904).
[7] *Ibid.*, [3], **31**, 30 (1904).
[8] Ber. d. chem. Ges., **35**, 3695.
[9] Sachs u. Loevy : Ber. d. chem. Ges., **36**, 1588 (1903). Grignard : Compt. rend., **136**, 815 (1903).

$$COCl_2 + 3RMgX = \begin{matrix} R \\ R \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} OMgX \\ R \end{matrix} + 2MgX.Cl,$$

and

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} OMgX \\ R \end{matrix} + H_2O = R_2C(OH) + Mg(OH)X.$$

Other reactions may also take place simultaneously, giving rise to ketones and secondary alcohols, as well as to unsaturated alcohols formed from them by loss of water.[1]

Thiophosgene, $CSCl_2$, also reacts readily with organo-magnesium halides.[2]

As in his principal article[3] Grignard gives a general review of the subject up to that time, it will be followed closely in the remainder of this report, for much of the later work is but a development along lines laid down by him, or describes syntheses which he failed to carry out.

Before going further it may be well to give, in detail, the general method of work as described by Grignard. After the solution of the organo-magnesium compound has been prepared as stated (p. 305) the balloon flask containing it is cooled with water and the required amount of aldehyde, ketone, etc., dissolved in anhydrous ether, is allowed to drop into it slowly. A return-condenser is attached to the flask, for the reaction is quite energetic at first, each drop producing a hissing noise. The solid that separates sometimes dissolves, but may remain as a crystalline or viscous layer at the bottom. When all of the reagent has been added the contents of the flask are kept boiling gently on the water-bath, or, if too viscous, allowed to stand several hours at the ordinary temperature. The mixture is then slowly poured upon crushed ice and the magnesium hydroxide dissolved by adding small portions of hydrochloric or acetic acid. Theoretically, it is necessary to add only 1 molecule of acid, but a little more is always needed to make the liquid slightly acid. The ethereal layer is then decanted; if the product which is formed, for instance an alcohol, is soluble in water, the aqueous layer is distilled with steam and the alcohol separated from the distillate by means of potassium carbonate. The ethereal layer is washed with dilute sodium bicarbonate, to avoid the precipitation of magnesium, then with sodium acid sulphite to remove any aldehyde or ketone

[1] Grignard: *Loc. cit.*
[2] Sachs u. Loevy: *Loc. cit.*
[3] Ann. Chim. Phys., [7], **24**, 433 (1901).

that may remain. The ether is then driven off, with suitable precautions and the residue is distilled or otherwise purified, according to its nature. Small amounts of polymerization-products are usually formed.

When treated with water, the organo-magnesium halides yield saturated hydrocarbons according to the equation :

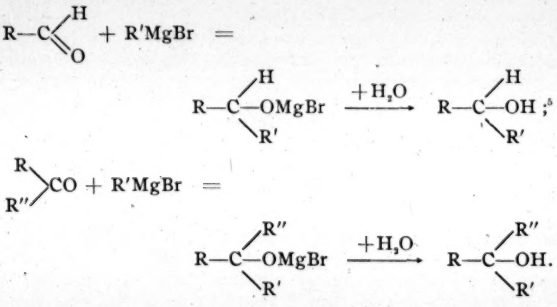
$$RMgX + H_2O = RH + Mg(OH)X.^1$$

This reaction has been suggested as a means of detecting the hydroxyl group.[2]

Another way to make saturated hydrocarbons is by the reaction :

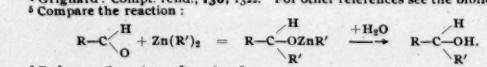
$$(CH_3)_2SO_4 + RMgBr = RCH_3 + CH_3SO_4.MgBr.^3$$

Aldehydes and ketones yield secondary and tertiary alcohols, respectively,[4] as shown by the equations :



By analogous reactions phenols can be made.[6] Thiophenols and selenophenols are prepared by the action of sulphur and selenium,[7] respectively, on organo-magnesium compounds. The corresponding disulphides and diselenides are formed at the same time. These reactions led to a study of the action of

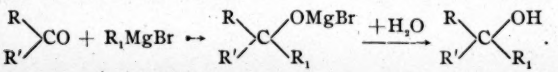
[1] Grignard : *Loc. cit.*
[2] Tschugaeff : Ber. d. chem. Ges., **35**, 3912.
[3] Werner u. Zilkens : *Ibid.*, **36**, 2116. Houben : *Ibid.*, **36**, 3083 ; **37**, 488. Werner : *Ibid.*, **36**, 3618.
[4] Grignard : Compt. rend., **130**, 1322. For other references see the bibliography.
[5] Compare the reaction :



[6] Bodroux : Compt. rend., **136**, 158.
[7] Taboury : Bull. Soc. Chim., [3], **29**, 761 ; **31**, 581, 646, 1183.

oxygen on the organo-magnesium halides[1] and it was found that primary alcohols and phenols could be made in this way. Theoretically, the simplest method for the preparation of primary alcohols is by means of formic aldehyde and this has been accomplished by the action of its polymer, trioxymethylene, on the magnesium compound.[2]

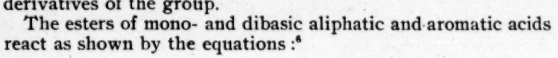
It is interesting to compare the reactions with the different classes of oxygen compounds. The aldehydes have already been mentioned. The ketones react in much the same way:[3]

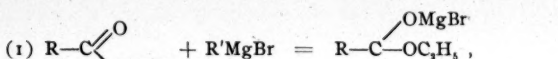


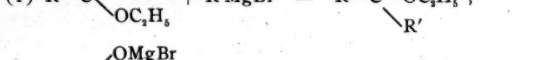
Diketones[4] yield the corresponding pinacones.

The cyclic ketones[5] react normally, as, in general, do other derivatives of the group.

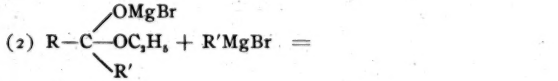
The esters of mono- and dibasic aliphatic and aromatic acids react as shown by the equations:[6]







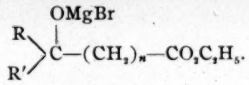
and



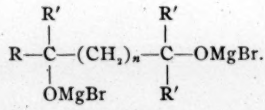
With the esters of ketone acids, either the ketone group acts alone or the carbonyl and carboxyl groups act simultaneously.[7]

[1] Bouveault: *Ibid.*, [3], **29**, 1051 (1903).
[2] Grignard et Tissier: Compt. rend., **134**, 107 (1902).
[3] Grignard: Ann. Chim. Phys., [7], **24**, 433 (1901).
[4] Zelinsky: Ber. d. chem. Ges., **35**, 2138 (1902).
[5] Zelinsky u. Gutt: *Ibid.*, **35**, 2140 (1902).
[6] Grignard: Compt. rend., **132**, 136. Masson: *Ibid.*, **132**, 483. Béhal, Tiffeneau et Sommelet: *Ibid.*, **132**, 480. Valeur: *Ibid.*, **132**, 833.
[7] Grignard: Ann. Chim. Phys., [7], **27**, 548 (1902).

In no case was a compound formed by the action of the carboxyl group alone. We first obtain



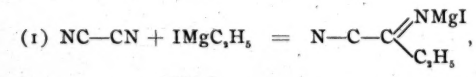
If this be treated with water the ester of an alcohol acid is formed; in some cases it at once combines with more of the magnesium organic halide, giving

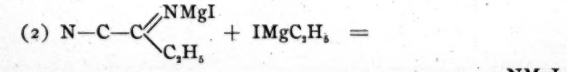


This yields a bitertiary glycol when treated with water.

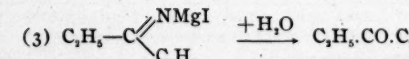
Unsaturated hydrocarbons are frequently formed in working with compounds containing a large number of carbon atoms, on account of the loss of water by the alcohols which are originally produced. This was first noticed by Grignard and was made use of by other investigators.[1]

Ketones can be made by the action of cyanogen or nitriles upon the organo-magnesium halides.[2]





and



Similarly:

[1] Ann. Chim. Phys., [7], **24**, 433 (1901). Houben, Hell and Bauer, Hell and Stockmayer, Klages and Heilmann, Thiele and Balhorn, etc. See bibliography.
[2] Blaise: Compt. rend., **132**, 38.

$$RCN + BrMgR' = R{-}C(=NMgBr){-}R'.$$

This, with dilute acids, yields R.CO.R'.

Béis made ketones by the reactions :[1]

$$(1)\ RCONH_2 + 2Mg\langle{}^{R'}_{X} = R{-}C(OMgX){-}NHMgX + R'H,$$

$$(2)\ R{-}C(OMgX){-}NHMgX + 2H_2O =$$

$$R{-}C(OH){-}NH_2 + MgX_2 + Mg(OH)_2,$$

$$(3)\ R{-}C(OH){-}NH_2 = R{-}C(=O){-}R' + NH_3.$$

Several different ways of making aldehydes have been discovered. Gattermann and Maffezeoli[2] used the reaction :

$$CH_3C_6H_4MgBr + HCOOC_2H_5 = BrMgOC_2H_5 + CH_3C_6H_4.CHO;$$

Bouveault[3] allowed dimethylformamide to react with magnesium organic halides according to the equations :

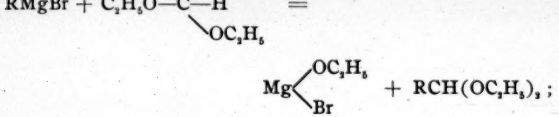
$$HCON(CH_3)_2 + RMgX = H{-}C(OMgX){-}N(CH_3)_2;$$

$$H{-}C(OMgX){-}N(CH_3)_2 + H_2O + (H_2SO_4) =$$

$$RCHO + NH(CH_3)_2 + MgXOH + (H_2SO_4).$$

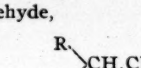
[1] Compt. rend., **137**, 575 (1903).
[2] Ber. d. chem. Ges., **36**, 4152 (1903).
[3] Compt. rend., **137**, 756 (1903).

With the esters of orthoformic acid we get the reactions:[1]

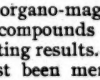


$$RCH(OC_2H_5)_2 + H_2O + (HCl) \rightarrow RCHO.$$

Starting with $RCO.CH_2.OC_2H_5$ and R'MgBr we can get

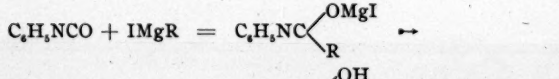


this yields the aldehyde,



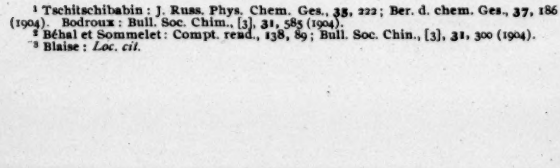
when dehydrated by heating with anhydrous oxalic acid.[2]

The reactions of the organo-magnesium halides with different classes of nitrogen compounds have been studied, in some cases with very interesting results. The production of ketones and aldehydes has just been mentioned. Ketone esters are obtained from cyan esters, for instance:



and this, with water, gives $C_2H_5O_2C—CH_2CO.C_2H_5$.

When isocyanates are used we get anilides:[3]



[1] Tschitschibabin: J. Russ. Phys. Chem. Ges., **38**, 222; Ber. d. chem. Ges., **37**, 186 (1904). Bodroux: Bull. Soc. Chim., [3], **31**, 585 (1904).
[2] Béhal et Sommelet: Compt. rend., **138**, 89; Bull. Soc. Chin., [3], **31**, 300 (1904).
[3] Blaise: *Loc. cit.*

Anilides were also prepared from esters.[1]

$$2RNHMgI + R'.COOR'' = Mg\begin{matrix}OR''\\I\end{matrix} + R'-\underset{\displaystyle OMgI}{\overset{\displaystyle NHR}{\underset{|}{\overset{|}{C}}}}-NHR.$$

This, with dilute hydrochloric acid, yields

$$R'C\begin{matrix}=O\\NHR\end{matrix} + MgICl + RNH_2.$$

Sachs and Loevy studied the reaction with the mustard oils,[2] obtaining, as we should expect, the thioanilides, or in general, the thioacylamines, R.NHCSR'.

Hydroxylamine derivatives are formed when nitrogen peroxide, or nitro compounds, are allowed to act upon organomagnesium halides :

$RNO_2 + R'MgX \rightarrowtail RR'N.OH$;[3]

$C_2H_5MgI + NO_2 \rightarrowtail (C_2H_5)_2NO.MgI \rightarrowtail (C_2H_5)_2N.OH$.[4]

With nitric oxide we have the reaction :

$$NO = O{=}N{-}N{=}O + C_6H_5MgBr \rightarrowtail O{=}N{-}N\begin{matrix}OMgBr\\C_6H_5\end{matrix} \rightarrowtail O{=}N{-}N\begin{matrix}OH\\C_6H_5\end{matrix}.$$[5]

A number of more complex reactions have been carried out with other nitrogen compounds,[6]

The Grignard reaction has been found to be applicable to the formation of alkyl and aryl derivatives of certain metals. Compounds of tin,[7] lead and mercury,[8] thallium[9] and silicon[10] have been made. A few of these are represented by the formulas,

$Sn(C_6H_5)_4$, $Sn(C_6H_5CH_2)_3Cl$, $Pb(C_6H_5)_4$, $Hg(C_6H_5)_2$, $(C_6H_5)_2SiO$, C_6H_5SiOOH, etc.

[1] Bodroux : Compt. rend., **138**, 1427.
[2] Ber. d. chem. Ges., **36**, 585 ; **37**, 874.
[3] Moureu : Compt. rend., **132**, 837 (1901).
[4] Wieland : Ber. d. chem. Ges., **36**, 2315 (1903).
[5] Sand u. Singer : Ann. Chem. (Liebig), **329**, 190 (1903).
[6] See bibliography.
[7] Pfeiffer u. Schnurmann : Ber. d. chem. Ges., **37**, 319.
[8] Pfeiffer u. Truskier : *Ibid.*, **37**, 1125.
[9] Meyer u. Bertheim : *Ibid.*, **37**, 2051.
[10] Dilthey u. Eduardoff : *Ibid.*, **37**, 2051.

Some of the typical reactions are given :

$$SnBr_4 + C_6H_5MgBr = Sn(C_6H_5)_4 + 4MgBr_2,$$

$$SnCl_4 + C_6H_5CH_2MgCl \rightarrowtail (C_6H_5CH_2)_3SnCl,$$

and

$$2PbCl_2 + 4C_6H_5MgBr = Pb + Pb(C_6H_5)_4 + 2MgCl_2 + 2MgBr_2.$$

Similar reactions take place with the trichloride and oxychloride of phosphorus.[1]

$$PCl_3 + C_6H_5MgBr \rightarrowtail P(C_6H_5)_3,$$

and

$$POCl_3 + C_6H_5MgBr \rightarrowtail (C_6H_5)_2PO.OH + (C_6H_5)_3PO.$$

This comparatively brief summary of the work that has been done in this field will give at least an idea of the possibilities of the Grignard reaction. Only its more general applications have been discussed, but a study of the bibliography will show how wide these are and will suggest new lines of investigation.

In the bibliography which follows an attempt has been made to give references to all articles bearing on the subject, including those in which the method was used to prepare compounds for other lines of work. It is brought down to February 21, 1905.

BIBLIOGRAPHY.

LIEBIG'S ANNALEN DER CHEMIE.

LÖHR : Ueber Alkylverbindungen des Cadmiums und des Magnesiums. **261,** 48 (1891) ; (Magnesium : S. 72.)

FLECK : Ueber Magnesium-Alkyle ; **276,** 129 (1893).

WAGA : Ueber Magnesium-Diphenyl ; **282,** 320 (1894).

SAND u. SINGER : Stickoxyd und das Grignard'sche Reagens ; **329,** 190 (1903).

ANNALES DE CHIMIE ET DE PHYSIQUE. 7me Série.

GRIGNARD : Sur les combinaisons organomagnésiennes mixtes et leurs application a des synthèses d'acides, d'alcools et d'hydrocarbures ; **24,** 433 (1901).

GRIGNARD : Action des combinaisons organomagnésiennes mixtes sur les éthers d'acides cétoniques ; **27,** 548 (1902).

COMPTES RENDUS.

BARBIER : Synthèse de quelques alcools tertiares. Diphenylcarbinol ; **128,** 110 (1899).

GRIGNARD : Sur quelques nouvelles combinaisons organométalliques du magnésium et leur application a des synthèses d'alcools et d'hydrocarbures ; **130,** 1322 (1900).

[1] Sauvage : Compt. rend., **139,** 674.

BLAISE : Nouvelles réactions des dérivés organométalliques ; **132,** 38 (1901).

GRIGNARD : Action des éthers d'acides gras monobasiques sur les combinaisons organomagnésiennes mixtes ; **132,** 336 (1901).

BLAISE : Nouvelle réactions des dérivés organométalliques (II) éthers α-alcoyl-β-cétoniques ; **132,** 478 (1901).

BÉHAL : Action des dérivés organométalliques sur les éthers sels; **132,** 480 (1901).

BÉHAL et TIFFENEAU : Sur un isomère de l'anéthol et sur la constitution de ce dernier ; **132,** 561 (1901).

MASSON : Synthèses d' alcools tertiares de la série gras; **132,** 483 (1901).

GRIGNARD : Sur les combinaisons organomagnésiennes mixtes ; **132,** 558 (1901).

TISSIER et GRIGNARD : Action des chlorures d'acides et des anhydrides d'acides sur les composés organométalliques du magnésium ; **132,** 683 (1901).

VALEUR : Action des éthers d'acides bibasiques sur les composés organométalliques ; **132,** 833 (1901).

TISSIER et GRIGNARD : Sur les composés organométalliques du magnésium ; **132,** 835 (1901).

MOUREU : Nouvelles réactions des composés organomagnésiens ; **132,** 837 (1901).

BLAISE : Sur les dérivés éthero-organomagnésiens ; **132,** 839 (1901).

BLAISE : Nouvelles réactions des dérivés organométalliques (III) Ethers β-cétoniques non-substitués ; **132,** 978 (1901).

TISSIER et GRIGNARD : Sur les composés organomagnésiens aromatiques ; **132,** 1182 (1901).

BLAISE : Nouvelles réactions des dérivés organométalliques. Synthèse des cétones ; **133,** 1217 (1901).

GRIGNARD et TISSIER : Action des combinaisons organomagnésiennes mixtes sur le trioxyméthylène. Synthèses d'alcools ; **134,** 107 (1902).

BLAISE : Nouvelles réactions des dérivés organométalliques ; **134,** 551 (1902).

GRIGNARD : Action des combinaisons organomagnésiennes sur les éthers β-cétoniques ; **134,** 849 (1902).

MASSON : Synthèse de quelques alcools tertiares. Diphénylcarbinol ; **135,** 533 (1902).

GRIGNARD : Action des combinaisons organomagnésiennes mixtes sur les éthers d'acides cétoniques ; **135,** 627 (1902).

BODROUX : Sur une méthode de transformation des dérivés monochlorés et monobromés des hydrocarbures en dérivés monoiodés; **135,** 1350 (1902).

BODROUX : Sur un mode de formation des phénols; **136,** 158 (1903).

MEUNIER : Action des combinaisons organomagnésiennes mixtes sur les corps a fonctions azotées ; **136,** 758 (1903).

GRIGNARD : Action du phosgène sur les combinaisons organomagnésiennes mixtes ; **136,** 815 (1903).

BODROUX : Dérivés organométalliques des hydrocarbures aromatiques dihalogenés dans le noyau. Action de l'iode ; **136,** 1138 (1903).

GRIGNARD : Action du chlorure d'éthyloxalyle sur les combinaisons organomagnésiennes mixtes ; **136,** 1200 (1903).

GRIGNARD : Sur le mode de scission des combinaisons organomagnésiennes mixtes. Action de l'oxyde d'éthylène ; **136**, 1260 (1903).

TIFFENEAU et DELANGE : Fixation anormale du trioxyméthylène sur certains dérivés organomagnésiens aromatiques ; **137**, 573 (1903).

BÉIS : Actions des composés organomagnésiens mixtes sur les amides. Nouvelle méthode de préparation de cétones ; **137**, 575 (1903).

MEUNIER : Sur l'emploi de l'amalgame de magnésium en chimie organique ; **137**, 714 (1903).

KLING : Action des dérivés organomagnésiens sur l'acetol et ses éthers-sels ; **137**, 756 (1903).

BOUVEAULT : Nouvelle méthode de préparation des aldéhydes ; **137**, 987 (1903).

BÉHAL et SOMMELET : Sur une méthode de synthèse des aldéhydes ; **138**, 89 (1904).

BODROUX : Synthèse d'aldéhydes aromatiques ; **138**, 92 (1904).

GRIGNARD : Nouveau procédé de synthèse d'alcools tertiaires au moyen des combinaisons organomagnésiennes ; **138**, 152 (1904).

HALLER et GUYOT : Action du bromure de phénylmagnésium sur l'anthraquinone. Dihydrure d'anthracène γ-dihydroxylé-γ-diphénylé symétrique ; **138**, 327 (1904).

BODROUX : Sur une méthode générale de synthèse des aldéhydes : **138**, 700 (1904).

HAMONET : Préparation des éthers-oxydes au moyen des composés magnésiens et des éthers méthyliques halogénés XCH_2OR ; **138**, 813 (1904).

HAMONET : Éthers oxydes halogénés $RO(CH_2)_nX$; leurs composés magnésiens $RO(CH_2)_nMgX$; nouvelles synthèses dans la série du tétraméthylène ; **138**, 975 (1904).

TABOURY : Action du soufre et du sélénium sur les combinaisons organomagnésiennes des hydrocarbures aromatiques mono- et dihalogénés dans le noyau ; **138**, 982 (1904).

BÉIS : Action des composés organomagnésiens mixtes sur la phthalimide et la phénylphthalimide ; **138**, 987 (1904).

GRIGNARD : Action du magnésium et des combinaisons organomagnésiennes sur le bromphénetol ; **138**, 1048 (1904).

BOUVEAULT : Application de la réaction de Grignard aux éthers halogénés des alcools tertiaires ; **138**, 1108 (1904).

HALLER et GUYOT : Sur le γ-diphénylanthracène et le dihydrure de γ-diphénylanthracène symétriques ; **138**, 1251 (1904).

MOUREU et DELANGE : Aldéhydes acétyléniques. Nouvelle méthode de préparation ; action de l'hydroxylamine ; **138**, 1339 (1904).

BODROUX : Nouvelle méthode de préparation des anilides ; **138**, 1427 (1904).

HAMONET : Synthèses dan la série pentaméthylénique : diamyline du pentanediol ; dibrompentane et diiodopentane-1,5 ; **138**, 1609 (1904).

BÉHAL et TIFFENEAU : Sur quelques éthers phénoliques a chaine pseudoallylique, $R-C(CH_3)CH_2$; **139**, 139 (1904).

SABATIER et MAILHE ; Synthèses de divers alcools dans la série du cyclohexane ; **139**, 343 (1904).

TIFFENEAU : Synthèse de l'estragol et des dérivés aromatiques à chaine non saturés ; **139**, 481 (1904).

AUGER et BILLY : Action des solutions organomagnésiennes sur les dérivés halogénés du phosphore, de l'arsenic et de l'antimoine ; **139,** 597 (1904).

SAUVAGE : Action des chlorures de phosphore sur les combinaisons organomagnésiennes de la série aromatique ; **139,** 674 (1904).

GUYOT ET CATEL : Contribution à l'étude des dérivés du benzodihydrofurfurane ; **140,** 254 (1905).

BULLETIN DE LA SOCIÉTÉ CHIMIQUE, 3me Série.

GRIGNARD : Action des combinaisons organomagnésiennes sur les méthylnaphthylcétones ; **25,** 497 (1901).

BOUVEAULT et BONGERT : Synthèses de cétones et d'acylacétones en partant des éthers C-acylacétiques ; **27,** 1083 (1902).

WUYTS et COSYNS : L'action du soufre sur les composés organomagnésiens ; **29,** 689 (1903).

MEUNIER : Action des combinaisons organomagnésiennes mixtes sur les corps à fonctions azotées ; **29,** 314 (1903).

TABOURY : Action du soufre et du sélénium sur le bromure de phénylmagnésium et sur le bromure d'α-naphthylmagnésium ; **29,** 761 (1903).

GRIGNARD : Sur le mode de scission des combinaisons organomagnésiennes mixtes ; **29,** 944 (1903).

GRIGNARD : Action du chlorure d'éthyloxalyle sur les combinaisons organomagnésiennes ; **29,** 948 (1903).

GRIGNARD : Sur l'alcool phényléthylique primaire ; **29,** 953 (1903).

GRIGNARD : Sur une mode de préparation du diéthylacétacétate de méthyle ; **29,** 954 (1903).

BOUVEAULT : Sur l'aldéhyde hexahydrobenzoique, hexahydroacétophénone et l'alcool secondaire correspondant ; **29,** 1049 (1903).

BOUVEAULT : Action de l'oxygène dur les dérivés organo-halogènemagnésiens ; **29,** 1051 (1903).

KLING : Action des dérivés organo-magnésiens sur l'épichlorhydrine ; **31,** 14 (1904).

KLING : Action des dérivés organo-magnésiens sur l'acétol et ses éthers-sels ; **31,** 16 (1904).

BODROUX : Dérivés organo-magnésiens des hydrocarbures aromatiques dihalogénés dans le noyau : Action de l'anhydride carbonique : **31,** 24 (1904).

BODROUX : Dérivés organo-magnésiens des oxydes phénoliques monobromés : Action de l'anhydride carbonique ; **31,** 30 (1904).

BODROUX : Oxydation des combinaisons mixtes. Synthèse des phénols; **31,** 33 (1904).

BÉHAL et SOMMELET : Méthode de synthése des aldéhydes ; **31,** 300 (1904).

BÉHAL : Sur quelques dérivés campholèniques ; **31,** 461 (1904).

TABOURY : Action du soufre sur les dérivés organomagnésiens des hydrocarbures aromatiques dihalogénés dans le noyau ; **31,** 581, 646 (1904).

BODROUX : Sur une méthode générale de synthèse des aldéhydes ; **31,** 585 (1904).

LOCQUIN : Sur l'alcool isoamylique synthétique et l'alcool amylique du commerce ; **31,** 599 (1904).

BOUVEAULT et BLANC: Transformation des acides monobasiques saturés dan les alcools primaires correspondants; **31**, 666 (1904).

GRIGNARD: Action des combinaisons organomagnésiennes sur leurs dérivés carboxylés; Nouvelle méthode de synthèse d'alcools tertiaires; **31**, 751 (1904).

HALLER et GUVOT: Synthèses dans da série anthracènique; **31**, 795, 979 (1904).

TABOURY: Sur quelques sulfures phénoliques mixtes; **31**, 1183 (1904).

BERICHTE DER DEUTSCHEN CHEMISCHEN GESELLSCHAFT.

ZELINSKY: Ueber eine Synthese der cyclischen tertiären Alkohole mit Hülfe von Magnesiumhalogenalkylen; **34**, 2877 (1901).

ZELINSKY: Ein Beitrag zur Kenntniss der Synthese von cyclischen tertiären Alkoholen mit Hülfe von magnesiumorganischer Verbindungen; **34**, 3590 (1901).

ZELINSKY: Ueber das Verhalten von Diketonen zu Magnesium-organischer Verbindungen; **35**, 2138 (1902).

ZELINSKY u. GUTT: Ersatz von Zink durch Magnesium bei einigen synthetischen Reactionen; **35**, 2140 (1902).

HOUBEN u. KESSELKAUL: Synthesen von Carbonsäuren; **35**, 2519 (1902).

KLAGES: Zur Kenntniss der Styrole; **35**, 2632, 3506 (1902).

KLAGES; Synthese diarylirter Aethylene; **35**, 2646 (1902).

KLAGES: Ueber das Phenylbutadiën; **35**, 2649 (1902).

ZELINSKY u. NAMJETKIN: Ueber die Synthese von Methyl-(1)-cyclopentanol-(1); **35**, 2683 (1902).

ZELINSKY u. MOSER: Ueber Ringschliessung mittels magnesiumorganischer Verbindungen—Eine Totalsynthese des Methylcyclopentans; **35**, 2684 (1902).

ZELINSKY: Ueber eine directe Synthese hexahydroaromatischer und überhaupt cyclischer Polymethylencarbonsäuren; **35**, 2687 (1902).

ZELINSKY: Synthese der Benzoesäure und der α-Toluylsäure als Vorlesungsversuch; **35**, 2692 (1902).

SAND u. SINGER: Mercuri-Verbindungen aus Terpineol und Dimethylheptenol: **35**, 3170 (1902).

HOUBEN u. KESSELKAUL: Synthesen mit Hülfe magnesiumorganischen Verbindungen; **35**, 3695 (1902).

MALMGREN: Synthesen in der Camphergruppe mittels Magnesiumpulvers; **35**, 3910 (1902).

TSCHUGAEFF: Magnesium-organische Verbindungen als Reagens auf die Hydroxylgruppe; **35**, 3912 (1902).

ZELINSKY: Ueber die Synthese der Menthancarbonsäure und der Camphancarbonsäure; **35**, 4415 (1902).

HELL u. BAUER: Aromatische Propenverbindungen; **36**, 204 (1903).

ZELINSKY: Ueber eine neue Synthese der Camphocarbonsäure; **36**, 208 (1903).

SACHS u. LOEVY: Ueber das Verhalten von Senfölen gegen magnesiumorganische Verbindungen; **36**, 585 (1903).

DIMROTH: Synthesen mit Diazobenzolimid; **36**, 909 (1903).

WEIGERT: Ueber organische Synthesen mittels Kohlenoxysulfid; **36**, 1007 (1903).

HELL u. BAUER: Ueber aromatische Propenverbindungen. Ueber *o*-Anethol; **36**, 1184 (1903).

SACHS u. LOEVY: Ueber magnesiumorganische Verbindungen. Einwirkung von Phosgen; **36**, 1588 (1903).

BAMBERGER u. BLANGEY: Synthese der Chinole; **36**, 1625 (1903).

WERNER u. ZILKENS: Ueber eine neue Synthese von Kohlenwasserstoffen; **36**, 2116 (1903).

WIELAND: Ueber die Einwirkung des Stickstoffdioxyds auf organische Magnesiumverbindungen; **36**, 2315 (1903).

MALMGREN: Synthese in der Camphergruppe mittels Magnesiumpulvers; **36**, 2608 (1903).

HOUBEN: Ueber die Einwirkung von Magnesium und Kohlensäure auf Allylbromid; Eine neue Synthese der Vinylessigsäure; **36**, 2897 (1903).

SCHROETER: Ueber die Einwirkung von Kohlensäure auf Phenylmagnesium; **36**, 3005 (1903).

HOUBEN: Eine neue Synthese von Kohlenwasserstoffen mittels magnesiumorganischer Verbindungen; **36**, 3083 (1903).

HOUBEN: Ueber die Einwirkung von Chlorkohlensäureester auf Alkylmagnesiumhaloide; **36**, 3087 (1903).

SACHS u. LOEVY: Berichtigung über Tribenzylcarbinol; **36**, 3236 (1903).

WERNER: Eine neue Synthese von Kohlenwasserstoffen mittels magnesiumorganischer Verbindungen; **36**, 3618 (1903).

GATTERMANN u. MAFFEZEOLI: Ueber die Darstellung von Aldehyden aus Organomagnesiumverbindungen; **36**, 4152 (1903).

FREUND: Zur Kenntniss des Cotarnins; Anwendung der Grignard'schen Reaction auf dasselbe; **36**, 4257 (1903).

BRÜHL: Neuere Versuche über Camphocarbonsaure; **36**, 4272 (1903).

EHRLICH u. SACHS: Die Darstellung von Triphenylmethanfarbstoffen aus Brommagnesiumdimethylanilin als Vorlesungsversuch; **36**, 4296 (1903).

TSCHITSCHIBABIN: Eine neue allgemeine Darstellungsmethode der Aldehyde; **37**, 186 (1904).

HELL u. STOCKMAYER: Ueber Anisyl-phenyl-propen; **37**, 225 (1904).

HELL u. BAUER: Aromatische Propenverbindungen; Diphenyl-propen und Phenyl-methyl-propen; **37**, 230 (1904).

PFEIFFER u. SCHNURMANN: Beitrag zur Darstellung von Alkyl- und Aryl-Zinnverbindungen; **37**, 319 (1904).

SACHS u. LUDWIG: Ueber die Einwirkung magnesiumorganischer Verbindungen auf alkylirte Phthalimide; **37**, 385 (1904).

HELL: Ueber eine einfache Bildung von Stilben, Mono-4-methoxystilben und α-Methylstilben; **37**, 453 (1904).

HOUBEN: Zur Synthese von Kohlenwasserstoffen mittels magnesiumorganischer Verbindungen und Methylsulfat; **37**, 488 (1904).

HOUBEN: Ueber die Einwirkung magnesiumorganischer Verbindungen auf Lactone; **37**, 489 (1904).

BÜNZLY u. DECKER: Ueber einige Ammoniumverbindungen; Synthese eine Oxydihydrobase; **37**, 575 (1904).

ACREE: Ueber α-Naphthyl-magnesium-bromid; **37**, 625 (1904).

KLAGES u. SAUTTER: Ueber optischactive Benzolkohlenwasserstoffe; **37**, 649 (1004).

BAUER: Zur Darstellung von Dialkylphthaliden; **37**, 735 (1904).

BRÜHL: Metallorganische Synthesen der Acylcampher; **37**, 746 (1904).

HARRIES u. WEIL: Ueber 2,6-Dimethyl-heptadiën-2,5-diozonid; **37**, 845 (1904).

TSCHITSCHIBABIN: Ueber den Hexahydro-*m*-toluylaldehyd; **37**, 850 (1904).

SACHS u. LOEVY: Ueber die Einwirkung von magnesiumorganischer Verbindungen auf die Senföle und Isonitrile; **37**, 874 (1904).

ACREE: Ueber *o*-, *m*-, und *p*-Tolyl-diphenyl-carbinol; **37**, 990 (1904).

WAGNER, MOYCHO u. ZIENKOWSKI: Zur Kenntniss des Camphers; **37**, 1032 (1904).

SCHROETER: β-Methyl-zimmtsäure; **37**, 1090 (1904).

PFEIFFER u. TRUSKIER: Zur Darstellung organischer Blei- and Quecksilberverbindungen; **37**, 1125 (1904).

HELL u. BAUER: Aromatische Propenverbindungen, IV; Isoeugenoläthyläther; **37**, 1128 (1904).

DILTHEY u. EDUARDOFF: Ueber die Darstellung von Phenylsiliciumverbindungen; **37**, 1139 (1904).

KLAGES u. HEILMANN: Arylirte Aethylene und ihre Reduction zu Arylparaffinen; **37**, 1447 (1904).

THIELE u. BALHORN: Ueber einen chinoïden Kohlenwasserstoff; **37**, 1463 (1904).

ODDO: Metallorganische Synthesen in der Camphergruppe; **37**, 1569 (1904).

SACHS u. STEINERT: Zur Kenntniss des *p*-Dimethylamino-benzaldehydes; **37**, 1733(1904).

ULLMANN u. SCHLAEPFER: Ueber Derivate des Hexaphenyl-*p*-xylols; **37**, 2001 (1904).

MEYER u. BERTHEIM: Alkylverbindungen des Thalliums; **37**, 2051 (1904).

TSCHELINZEFF: Ueber die Analogie zwischen den organischen Sauerstoff und Stickstoff-Verbindungen; **37**, 2081 (1904).

HEIDE: Diazoessigester und Systeme mit conjugirten Doppelbindungen; **37**, 2101 (1904).

ROSENHEIM u. SINGER: Die Darstellung von Alkylsulfinsäuren; **37**, 2152 (1904).

BRÜHL: Untersuchungen in der Camphergruppe, I; **37**, 2156, 2163 (1904).

KLAGES: Zur Kenntniss der Styrole; **37**, 2301 (1904).

ULLMANN u. ENGI: Ueber 9-Diphenylxanthen; **37**, 2367 (1904).

DILTHEY u. LAST: Ueber die Einwirkung von Arylmagnesiumhalogeniden auf Dicarbonsäuren; **37**, 2639 (1904).

BUSCH: Ueber das Verhalten magnesiumorganischer Verbindungen zu Benzylanilin; **37**, 2691 (1904).

ACREE: Ueber einige Synthesen mit Hülfe von Phenylnatrium und Alkylmagnesiumbromiden; **37**, 2753 (1904).

BUNZLY u. DECKER: Ueber Xanthonium- und Thioxanthonium-Verbindungen; **37**, 2931 (1904).

SACHS u. SACHS: Das Verhalten tertiärer Amine gegen magnesiumorganischer Verbindungen; **37**, 3088 (1904).

BAEYER u. VILLIGER: Dibenzalaceton und Triphenylmethan; **37**, 3191 (1904).

SACHS, v. WOLFF u. LUDWIG: Die Einwirkung magnesiumorganischer Verbindungen auf alkylierte Saccharine; **37**, 3252 (1904).

SACHS u. THONET: Ueber Oxyfuchsone; **37**, 3326 (1904).

FREUND: Versuche zur Herstellung von Alkaloïden der Isochinolinreihe; **37**, 3334 (1904).

DECKER u. PSCHORR: Ueber die Einwirkung von Benzylmagnesiumchlorid auf Cyclaminone; **37**, 3396 (1904).

FEHLENBERG: Zur Kenntniss der Einwirkung von Magnesiummethyljodid auf Mesityloxyd und Phoron; **37**, 3578 (1904).

HOUBEN: Die Uebertragung der Kolbe'schen Salicylsäuresynthese auf stickstoffhaltige Benzolabkömmlinge; **37**, 3978 (1904).

KLAGES: Ueber die Reduction ungesättigter Phenoläther durch Natrium und Alkohol; **37**, 3987 (1904).

STOERMER u. SIMON: Ueber geometrische Isomerie bei Derivaten des Diphenyl-äthyläthers; **37**, 4163 (1904).

HELL u. HOFFMANN: Ueber das 4-Methoxyphenyl-äthyl-carbinol; **37**, 4188 (1904).

FREUND: Verfahren zur Darstellung solcher Verbindungen, welche sich von den Pseudobasen durch Ersatz der Hydroxylgruppe gegen Kohlenwasserstoffreste herleiten; **37**, 4666 (1904).

FREUND u. BECK: Ueber eine Reihe neuer, vom Dihydroberberin sich herleitender Basen; **37**, 4673 (1904).

FREUND u. BECK: Einwirkung von Benzylmagnesiumchlorid auf Krystallviolet; **37**, 4679 (1904).

FRANKE u. KOHN: Die Einwirkung magnesiumorganischer Verbindungen auf β-Oxyaldehyde und auf Ketonalkohole; **37**, 4730 (1904).

THE JOURNAL OF THE RUSSIAN PHYSICAL-CHEMICAL SOCIETY.

KONOWALOFF: The synthesis of tertiary alcohols by means of organo-α-magnesium compounds; **34**, 26 (1902). See Centrabl., 1902, I, 1271.

ZELINSKY: Some facts about catalyzers; **35**, 399 (1903). See Centrabl., 1903, II, 277.

MENSCHUTKIN: The etherates of the halogen compounds of magnesium; **35**, 610 (1903). See Centrabl., 1903, II, 1237.

AMERICAN CHEMICAL JOURNAL.

KOHLER: Diphenylstyrylcarbinol; **29**, 352 (1903).

KOHLER: The reaction between unsaturated compounds and organic magnesium compounds: **31**, 643 (1904).

KOHLER and HERITAGE: The reactions between organic magnesium compounds and unsaturated compounds. II. Reactions with derivatives of cinnamic acid; **33**, 21 (1905).

KOHLER and JOHNSTIN: III. Reactions with compounds containing bromine; **33**, 35 (1905).

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.

TOUSLEY and GOMBERG: Some tri-*p*-tolylmethane derivatives; **26**, 1516 (1904).

THE LONDON CHEMICAL SOCIETY.

Proceedings.

MCKENZIE: Studies in asymmetric synthesis. The action of magnesium alkyl halides on the menthyl ester of benzoylformic acid; **20**, 178 (1904).

PICKLES AND WEIZMANN: The action of anhydrides on organomagnesium bromides. Part I. Action of phthalic anhydride on magnesium α-naphthyl bromide; **20**, 201 (1904).

FORSTER: Action of magnesium alkyl halides on camphor derivatives; **20**, 207 (1904).

Journal.

PERKIN: Experiments on the synthesis of the terpenes. Part I. Synthesis of terpin, inactive terpineol and dipentene; **85**, 654 (1904).

MCKENZIE: Studies in asymmetric synthesis. II. Action of magnesium alkyl haloids on menthyl benzoylformate; **85**, 1249 (1904).

FRANKLAND and TWISS: The Grignard reaction applied to the esters of hydroxy acids; **85**, 1666 (1904).

JONES and TATTERSALL: A new synthesis of isocaprolactone and certain derivatives; **85**, 1691 (1904).

MISCELLANEOUS.

PICKLES and WEIZMANN: The effect of anhydrides on organo-magnesium bromides. Part I. The action of phthalic anhydride on magnesium α-naphthyl bromide. Chem. News; **90**, 276 (1904).

FORSTER: Action of magnesium alkyl halides on derivatives of camphor; *Ibid.*, **90**, 278 (1904).

GRIGNARD: Rev. gén. des sc., 1903, 1040.

MUNDICI: The Gattermann reaction for the synthesis of aromatic aldehydes. Application to *p*-xylene; Gazz. chim. ital., **34**, II, 114 (1904).

ZELINSKY: The preparation of organic acids from petroleum. D. R. P. 151,880.

FR. BAYER: Verfahren zur Darstellung von Aldehyden; D. R. P. 157,573.

KLAGES: Organische Synthesen mit Hilfe der Grignardscher Reagens; Chem. Ztg., **29**, 19 (1905). A review of the subject.

MAMELI: Action of magnesium ethyl iodide on piperonal. Atti Accad. Lincei., [5], **13**, II, 315 (1904).

C. E. WATERS.

OBITUARY.

ALFRED HENRY ALLEN.

Alfred H. Allen, F.C.S., F.I.C., was born at Southwark, London, January 17, 1846, and died at Sheffield, July 14, 1904. He received his professional education at the College of Chemistry and Agriculture, Kennington and at the Royal

College of Chemistry and School of Mines (now the Royal College of Science), under Hofmann, Tyndall and Percy and at University College, London. Shortly afterwards he settled in Sheffield. Allen's activity was many-sided, he was a successful teacher, was Borough and County Analyst and had a large private practice. His time and energy were given ungrudgingly to the service of the Society of Public Analysts, Institute of Chemistry and Society of Chemical Industry, in each of which he held high office for many years. Allen is, perhaps, best known in this country for his "Commercial Organic Analysis," which is easily the standard work on its subject. It is not a mere compilation, but contains the results of numerous original investigations made by the author and his assistants. He also wrote "Chemistry of the Urine," 1895, embodying his study of diabetes, from which he was suffering; in addition he was a frequent contributor to the analytical and technical journals. Allen's geniality and kindliness were combined with a wonderful memory, keenness of intellect and great ability for the rapid grasp of intricate questions.

REVIEWS.

MATERIALIEN DER STEREOCHEMIE. In Form von Jahresberichten. II Bände. Bearbeitet von C. A. Bischoff. 1904. pp. cxxxvi + 1977. Braunschweig: Vieweg und Sohn.

This work may be considered as a supplement to the two volumes of Bischoff's "Handbuch der Stereochemie," which have previously been reviewed.[1]

The book is in two volumes, of about two thousand pages and is made up of nine annual reports on stereochemistry, embracing the years 1894–1902. As its name implies it is intended chiefly for reference and maintains the cyclopedic character of the original "Handbuch."

Each year's report is divided into four sections, treating of general stereochemistry, optical isomerism, the geometrical isomerism of optically inactive bodies and the relations between positions in space and chemical reactions.

Under the section of general stereochemistry are included monographs and special publications dealing with stereochemical problems. The literature on the optical rotation of active organic compounds is very thoroughly reviewed in the second section. A systematic enumeration of the many examples of geometrical isomerism is given in section III. Inorganic compounds, occurring in more than one form, are also given here. Section IV., which treats of space relations in chem-

[1] THIS JOURNAL, 16, 475; 17, 725.

ical reactions, also includes a list of all known ring formations, organic and inorganic. Separate chapters in this section are devoted to molecular rearrangements, substitution- and addition-reactions, "Abspaltungen" und "Verkettungen."

Those who have not followed closely the progress of stereochemistry will be surprised to learn that so extensive a work could be written upon investigations in this subject, concerning which nothing was heard twenty years ago.

In some chapters the literature references are very complete, while in others they are decidedly lacking. One would not expect to see the American literature on molecular rearrangements completely ignored; more attention to it would greatly increase the value of the book. No references are given to the numerous publications on this subject by Stieglitz, Ransom and Wheeler and his co-workers, which have appeared since 1894.

The reviewer observed several typographical errors, as was to be expected in a work of such magnitude. On page 1203 the formula of *formylphenylessigester* is represented as HCO. $(C_6H_5)CHCOOC_6H_5$ instead of $HCO(C_6H_5)CHCOOC_2H_5$. The names of American writers have been misspelled in many instances, as is of common occurrence in German books.

Regardless of defects in the work, few chemists will fail to find it suggestive. Those who are especially interested in stereochemistry will find the book indipensable.

T. B. JOHNSON.

A SYSTEMATIC HANDBOOK OF VOLUMETRIC ANALYSIS, or the Quantitative Estimation of Chemical Substances by Measure, Applied to Liquids, Solids and Gases. Adapted to the Requirements of Pure Chemical Research, Pathological Chemistry, Pharmacy, Metallurgy, Manufacturing Chemistry, Photography, etc., and for the Valuation of Substances used in Commerce, Agriculture and the Arts. By FRANCIS SUTTON, F.I.C., F.C.S., Public Analyst for the County of Norfolk, etc. Ninth edition, revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 1904. pp. xii + 617.

Sutton's "Volumetric Analysis" has so long been a valued reference book that comment upon its general character is obviously superfluous. The present (ninth) edition has been printed from new plates and the text has been revised throughout. The size of the page is slightly larger and, although the number is less than in the last edition, the changes have resulted in a net increase of reading matter. These are so widely distributed throughout the text that a few only of the more striking can properly be enumerated.

The most extensive additions appear to be found in the paragraphs which treat of the examination of ammoniacal gas liquors, contributed by the Chief Inspector under the

Alkali-Works Regulation Acts and his assistant (pp. 77-82 and p. 502); in the section upon the azo dyes, nitro and nitroso compounds, etc., contributed by Dr. E. Knecht (pp. 366-367); in the description of Procter's modification of Hehner's method of estimating the hardness of waters (pp. 503-507) and in the account of the work of L. W. Andrews on the uses of potassium iodate (pp. 507-510). Other additions, as, for example, the description of the titration of iron by means of titanous chloride, the volumetric determination of magnesium, the extended description of the determination of free alkali in soap, or, on the other hand, the omission of certain methods which the author has come to distrust or consider obsolete (the Grossman-Böhlig method for the examination of salt-cake, for example) are at least an equally important part of the attempt to keep the handbook abreast of the times.

The index has been revised and extended and this work appears to have been well done, although one consults it in vain to discover the different uses made of titanous chloride, a somewhat unfamiliar agent as yet and also for the names of the originators of a considerable number of the processes mentioned in the text. But these are minor matters, the fact that the present edition has followed the eighth, after an interval of only four years, indicates the general high esteem in which the manual is held. H. P. TALBOT.

A TEXT-BOOK OF QUANTITATIVE CHEMICAL ANALYSIS BY GRAVIMETRIC, ELECTROLYTIC, VOLUMETRIC AND GASOMETRIC METHODS, with Seventy-two Laboratory Exercises giving the Analysis of Pure Salts, Alloys, Minerals and Technical Products. By J. C. OLSEN, A.M., PH.D., Professor of Analytical Chemistry in the Polytechnic Institute of Brooklyn. New York: D. Van Nostrand Company. 1904. pp. xix + 513.

This text-book is stated by the author to have been born of a spirit of discontentment with the previously existing manuals of analytical chemistry, because of the tendency of them to give special prominence to some one branch of the subject to the exclusion of others, thus necessitating reference, on the part of the thoughtful student, to a "very considerable number of text-books and journals." To avoid this perversion of time and energy the attempt has been made to present a work which shall accord to each branch of the subject—such as gravimetric, volumetric, electrolytic and gasometric analysis—a treatment which shall correspond with its relative importance from a practical standpoint and also to present a book which shall meet the author's own views as to desirable sequence of topics, while it likewise acquaints the student with the underlying

reasons for each step taken and develops his technical skill. It is avowedly written, in the first instance, as a text-book from which to teach.

The first two chapters deal with the general operations of chemical analysis and contain much timely advice; then follow thirteen chapters (154 pp.) dealing with gravimetric methods and including thirty-nine "laboratory exercises" (analytical procedures), which range in difficulty, though not strictly progressively, from the determination of water of crystallization to complete analyses of such alloys as Rose's metal, or those of complex silicates. Electrolytic methods are next dealt with in two chapters (27 pp.), followed by ten chapters (129 pp.) of volumetric methods, after which the analysis of iron, steel and coal, water analysis, the analysis of fats and oils, gas analysis and stoichiometry, each are treated in a single chapter (116 pp. in all); the whole ends with an appendix containing useful tables. Of the laboratory exercises not mentioned above, six comprise electrolytic methods, twenty-four volumetric procedures and the other two include the proximate analysis of coal and the analysis of illuminating gas.

Any attempt to produce a text-book of analytical chemistry which shall present a "thorough" and "comprehensive" view of the subject within the scope of the present volume seems, of itself, to invite criticism and it may fairly be questioned whether, looked at from a general standpoint, Professor Olsen has succeeded better than some of his predecessors in producing a well-balanced work. This should not imply, however, that there is not a great deal in his treatment of the subject that is worthy of the attention of all who are interested in the training of students in the art of chemical analysis, nor does it mean that the more experienced analyst will fail to find useful suggestions. Opinions must always differ as to the most desirable sequence in the presentation of topics to a class and, still more, as to the choice of detailed procedures. In these particulars the reader will quite likely find more to praise than to censure, but it is not so clear that in the chapters relating to specialized topics, such as gas analysis, water analysis, or the examination of oils, fats and waxes, the student will find such a treatment as will preclude that necessity for reference to more extended treatises which the author sought to avoid, nor does it seem reasonable that this should be so.

In the chapter devoted to stoichiometry, a phase of laboratory instruction, which is too often neglected is brought into desirable prominence and the subject-matter is presented in a

helpful way. Most of the procedures and explanations throughout the book are given with painstaking detail, but the work is uneven in this respect and in some cases, the directions, as given, would almost certainly lead to erroneous results. One such instance is found on p. 317, where, in the description of the determination of iron in its ores, the student is directed to add mercuric chloride solution to a *hot* solution containing a greater or less excess of stannous chloride. Reduction to metallic mercury would follow, which, in turn, would react upon the potassium dichromate used, obscuring the end-point of the titration.

The publishers cannot be congratulated upon the typography of this volume. Imperfect letters, inverted letters and crooked lines occur with unpleasant frequency throughout its pages. Other letters are missing, no less than five figures are lacking altogether in the logarithm table and the word phosphorus is frequently and uniformly misspelled throughout more than half of the volume. Carelessness in these matters has been noticeable in several recent works from different publishing houses, but in none to a greater extent than in this volume; it seems quite time that there should be a return to the old-time pride both in freedom from errors and in excellence of appearance.

But it may properly be said that Professor Olsen has contributed a volume to the literature of analytical chemistry which is of distinct interest from the teachers' standpoint and is worthy of the attention of his co-laborers.

H. P. TALBOT.

ELEMENTARY MANUAL FOR THE CHEMICAL LABORATORY. By LOUIS WARNER RIGGS, PH.D., Instructor of Chemistry in Cornell University. First edition. New York: John Wiley and Sons. 1904.

This is a laboratory guide for those students who need to cover the ground of general chemistry, qualitative analysis and volumetric analysis in one year. The author describes the chemical changes in qualitative analysis in terms of the electrolytic dissociation theory. The work on volumetric analysis precedes that on qualitative analysis; other teachers will agree with the author in preferring this sequence.

E. R.

THE INDUSTRIAL AND ARTISTIC TECHNOLOGY OF PAINT AND VARNISH. By ALVAH HORTON SABIN, Chemist, Edward Smith & Co. First Edition. New York: John Wiley and Sons. 1904. Cloth, 8vo. pp. vi + 364.

The author treats the subject more from the standpoint of the manufacturer and engineer than from that of the chemist.

The technology of varnish is the especial feature of the book and will be welcomed by those desiring general information on the subject. Varnish has usually been made behind closed doors and methods and mixtures guarded as trade secrets.

It is shown here, however, that the quality of the product is due to a knowledge of the requirements and to experience and care used in its manufacture.

The chapters on metal corrosion and protective coatings deal with the general causes of oxidation and means of prevention.

Results of an extended series of exposure tests of protective coatings, in salt and fresh water, are given and bear out, in general, the author's opinion regarding the durability of oleo resin varnishes and enamel paints.

The methods employed in making these tests can be studied to advantage, as it is difficult to secure comparable results in this line of investigation.

The thorough review of the early paint and varnish literature adds materially to the bibliography of the subject.

The author states that the present knowledge of the chemistry of resin gums is too indefinite to give a satisfactory method of analysis for oleo resin varnishes, so the analyst will gain but little new chemical data, except indications for lines of investigation.

Unfortunately, there is a lack of definite information on this subject and it is especially regretted that the author, with his knowledge as a chemist and manufacturer, should not have devoted more space to the chemistry of the fossil and recent resin gums and the changes which take place when they are melted and mixed with the oil in the varnish kettle.

This is a line of investigation of especial interest to the technical chemist and one which has received but scant attention in the literature.

The subject-matter is handled in a clear and readable manner, with evidence of the author's dry humor and pleasant personality; the index is good and the text free from typographical errors.

S. S. VOORHEES.